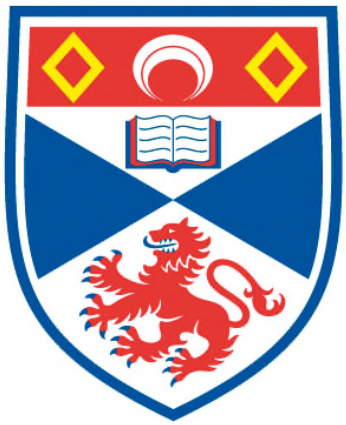
LANDUSE CHANGE AND ORGANIC CARBON EXPORTS FROM A PEAT CATCHMENT OF THE HALLADALE RIVER IN THE FLOW COUNTRY OF SUTHERLAND AND CAITHNESS, SCOTLAND

Shailaja Vinjili

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



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by

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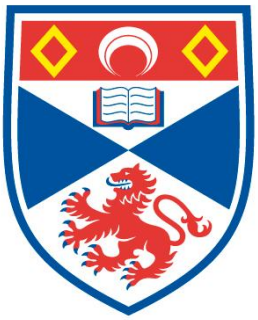
A thesis submitted in accordance with the requirements for the degree of Doctor of Philosophy



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August 2012

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ABSTRACT

Upland peat catchments are usually assumed to function as carbon sinks, however, there have been extensive studies witnessing increasing trends in concentrations and fluxes of organic carbon in UK rivers over the last few decades. A number of controls on dissolved organic carbon (DOC) release from peatlands, such as climatic changes and landuse management, have been proposed. This study examines the effects of land use and management on organic carbon exports in the Dyke catchment of the River Halladale (northern Scotland) with a nested catchment approach. This study provides insight into the processes controlling the DOC dynamics in the Dyke catchment, and the impact of disturbance caused by landuse changes such as afforestation and tree felling for restoration. The results from factor analysis, end-member mixing, absorbance (E4/E6), and hysteresis analyses on stream water chemistry from individual sub-catchments identified the major hydrological pathways during storm events, and based on these results, conceptual models were developed to explain DOC evolution during storm events. At all the sites studied, near-surface soil water was identified as the major controlling end-member for stream DOC concentrations.

The calculated annual flux of DOC from the Dyke catchment, up-scaled from the results of the individual sub-catchments, is 521.6 kg C ha^{-1} yr^{-1}, which is significantly (~5 times) higher than the previously published value (103.4 kg C ha^{-1} yr^{-1}) for the River Halladale catchment (Hope et al., 1997). In this study, it is shown that about 57 - 95% of the DOC export occur during 5 - 10% of the high flows, therefore, it is crucial that quantitative records of DOC export are developed using high frequency storm event measurements, as well as lower frequency low flow sampling.

Climatic changes related to precipitation, temperature, coupled with water yield capacity of the sub-catchments, are identified as significant controls on DOC fluxes, rather than landuse change, as the intact site releases more organic carbon per unit area compared to the disturbed and re-wetted site undergoing restoration. In addition, the results from this study provide landowners, policy makers and organisations with the evidence they require for initiating future peatland restoration works, as felling of forestry coupled with drain-blocking is shown to be an effective restoration technique that may help a catchment to eventually return to a near-pristine state.

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Glossary of acronyms used in this thesis:

Acronym/term	*Definition*	*Units*
OC	Organic Carbon	mg C L^{-1}
DOC	Dissolved Organic Carbon	mg C L^{-1}
POC	Particulate Organic Carbon	mg C L^{-1}
TOC	Particulate Organic Carbon	mg C L^{-1}
Discharge (Q)	Volume rate of streamwater flow	m^3 s^{-1}
Specific discharge	Discharge per unit area	m^3 s^{-1} km^{-2}
OC annual load	Organic carbon fluxes per annum = product of concentration, discharge and a conversion factor 'k'(C × Q × k).	kg C $year^{-1}$
OC annual yield	Organic carbon fluxes per unit area per annum = product of concentration, specific discharge and a conversion factor 'k'(C × Q × k).	kg C ha^{-1} $year^{-1}$
$A_{(360, 400,...)}$	Absorbance measured at specific wavelengths such as 360 nm, 400nm etc.	Abs units
E_4/E_6	Extinction ratio that indicates the degree of peat maturity. Generally determined using A_{465} and A_{665}.	
EMMA	End-member mixing analysis	
DO	Dissolved oxygen	mg L^{-1}
EC	Electrical conductivity	μS cm^{-1}

Chapter 1
INTRODUCTION

Peatlands are considered to be major carbon sinks globally, as the net primary production and accumulation of organic matter in these complex ecosystems exceeds the rate at which it is decomposed and exported. These carbon stores cover only 3% of the Earth's total land area (~450 million hectares) and the majority of this is in the northern hemisphere (Strack, 2008). Wetter climatic conditions in uplands are ideally suitable for peat formation, thus making them important terrestrial carbon stores. Boreal and subarctic peatlands store nearly 15 - 39% (~455 Pg C) of the world's soil carbon as peat (Gorham, 1991; Freeman *et al.*, 2001; Billett *et al.*, 2004). For example, upland blanket bogs in the UK represent a single large terrestrial carbon reserve that contain 3000 million tonnes of carbon, ~ 76% of which is stored in deep peats (>45cm) (Cannell *et al.*, 1993, 1999).

1.1. Landuse change

Many of the upland peatlands around the world have recently been disturbed by landuse changes such as drainage for forestry, agricultural improvement, peat extraction for fuel and horticulture, and burning. Such disturbances can significantly influence C cycling within peatlands, and lead them to become a source of carbon to atmospheric CO_2 and organic carbon to aquatic ecosystems (Waddington and Roulet, 1996; Dawson and Smith, 2007; Roulet *et al.*, 2007; Höper *et al.*, 2008). Changes of these kind in the equilibrium of land-atmosphere carbon exchange may provide a positive feedback mechanism to global climate warming (Pielke *et al.*, 2002; Matthews *et al.*, 2004; Smith, 2008; Arneth *et al.*, 2010).

Over the last two decades, the importance of restoration of degraded peatlands has been identified, and changes in land management practices that

may reduce carbon losses from disturbed peat soils (as they return to their pre-disturbance state) have been adopted. For example, in Germany, over 930,000 ha of peatlands have been drained for agriculture transforming them from a carbon sink to a carbon source which emits around 20 million t CO_2 eq $year^{-1}$ (Förster and Schafer, 2010). A peatland restoration strategy (MLUV MV, 2009) introduced in 2000 restored an area of 29,794 ha (10% of disturbed) of drained peatland by 2008, which means that emissions of about 300,000 t CO_2 eq $year^{-1}$ are prevented (Förster and Schafer, 2010). Recent studies in Canada by Waddington and Price (2000; 2001) reported a significant reduction in the magnitude of CO_2 losses (229 g C m^{-2}) to atmosphere when the peatland was restored and vegetation is re-established. In Sweden, 5% of the cutover peatland (about 500 – 1000 ha) are currently being restored with a potential to restore a further 30% (Vasander *et al.*, 2003). Similarly, 1800 ha of mined peatlands (6800 ha) in Canada have been restored and a projection of 3100 ha of excavated peat for restoration or reclamation by 2011 is reported (Quinty and Rochefort, 2003; Höper *et al.*, 2008). In Great Britain, 200,000 ha of the total peat bog (2.9 million ha) has undergone afforestation of which 3000 ha is now been restored (Anderson, 2010). A briefing from the IUCN UK Peatland Programme (2010) shows that delivering peatland restoration target of 600,000ha by 2015 in Scotland could provide at least 2.7 Mt CO_2 savings per year.

Landuse changes in UK peatlands are mainly related to developments in forestry, agriculture, and extraction for fuel and horticulture. Such changes in land management can be detrimental in terms of carbon losses from the peatlands, and may affect the hydrology and ecosystem function of peat (SNIFFER Report, 2011). Since the early 1970s, the UK has undergone extensive landuse change in the form of conifer plantations on drained peatlands, and may have significant impacts on catchment hydrology. Increased drainage of peatlands has cumulative effects such as subsidence, aeration of exposed peat

layers, and erosion which may result in increased organic carbon exports (Holden, 2006). In drained peats, a lower water table results in increased rates of organic matter decomposition as the aerated zone thickness increases (Frolking *et al.*, 2001; Holden *et al.*, 2004). Studies on DOC exports found that drained catchments release more discoloured and DOC-rich water than undisturbed catchments (Edwards *et al.*, 1987; Mitchell and McDonald, 1995; Moore, 1987). However, studies on the effects of a lower watertable on DOC exports demonstrate contradictory results; for example, while some studies observed an increase in DOC with lower water table (Tipping *et al.*, 1999), a decrease was reported by Freeman *et al.* (2004). In a long-term study, Chapman *et al.* (2010) have shown that drainage effects on DOC export vary between sites and depend on time since drainage, which suggests long-term changes in DOC production after drainage. Similarly, POC production and export have been reported to be significantly greater from drained peat catchments than intact peatlands (Holden, 2006; Holden *et al.*, 2007; Ramchunder *et al.*, 2009).

Afforestation of drained peatlands can influence DOC exports in many ways, including increased aeration due to the interception of rainwater in the canopy and evapotranspiration by trees which leads to exposure of various portions of peat to microbial oxidation; these may result in increased DOC production, CO_2 emission, and enhanced greenhouse effect (Cannell *et al.*, 1993). In addition, forest litter (*e.g.* leaves, twigs) can become a source of DOC production. This is demonstrated by Grieve and Marsden (2001) where higher DOC concentrations were found in forest soil pore water compared to moorland soil pore water. However, export rates of DOC from temperate forests were found to be lower than from moorland and grasslands (Hope *et al.*, 1994).

Recent realisations around the benefits of peatlands as carbon sinks and terrestrial reservoirs, and the introduction of the EU Habitats Directive, have driven a change in land use, and led to the conservation and restoration of these ecosystems. Consequently, there has been a steep decline in new plantations on thick peat since 1990, and measures towards deforestation of existing plantation on such peats and rewetting of previously drained areas are in place. The UK Forestry Commission has issued guidelines including a presumption against new plantation on peats (>1m in depth) (Patterson and Anderson, 2000). Restoration measures have been implemented to restore areas of damaged bogs by blocking the drainage ditches and/or felling of trees, and to protect adjacent areas of intact blanket bog from further damage (LIFE Peatlands Project, 2005). According to Defra Peat Project compendium (2008), more than 150 peatland restoration projects were operating in the UK at that time, with a primary focus on restoring ecological and hydrological function of sites. Of the restoration techniques, gully/drain-blocking and deforestation are the most common techniques adopted across the UK (Defra report, 2008).

The Flow Country of Caithness and Sutherland is the UK's largest blanket bog covering an area of ~ 400,000 ha, of which about 150,000 ha are 'severely affected' by landscape-scale drainage of the bog and non-native conifer planting. Consequently, water content in underlying peats was tremendously reduced resulting in subsidence and shrinkage of peat under the forest (Schothorst, 1982; Pyatt and John, 1989; Cannell *et al.*, 1993). Therefore, major initiatives to restore these degraded areas have been undertaken (LIFE Peatlands Project, 2005). As a part of EU- LIFE Peatlands project (1994-1998 and 2000-2006), RSPB have felled-to-waste 1774 of conifer plantation (in 9 years) and blocked hill drains (158km) and forest drains (42 km) in Forsinard Flows nature reserve in Flow Country. During this restoration project, between 1997 and present, non-native lodge-pole pine and sitka spruce (planted in 1980's) has

been felled from 2,200 ha of former blanket bog and drains have been blocked across 16,500ha of bog in Forsinard Flows (RSPB, 2011). This project has been designed to compare the DOC exports and DOC mobilisation processes from catchments under varying land uses in the Forsinard Flows area.

1.2. Organic carbon concentrations and fluxes

Over the last decade, increasing trends in riverine dissolved organic carbon exports have been widely reported in the northern hemisphere (Mulholland, 2002; Worrall *et al.*, 2004a; Monteith *et al.*, 2007; Dawson *et al.*, 2009), causing concerns about upland peatlands turning into sources of terrestrial carbon. The potential controls on fluvial organic carbon fluxes are identified as climatic changes (such as changes in precipitation, temperature and sulphur deposition), catchment characteristics, and land management practices (Hope *et al.*, 1994; Dawson *et al.*, 2001; Clark *et al.*, 2004; Soulsby *et al.*, 2006; Yoo *et al.*, 2006; Yallop and Clutterbuck, 2009).

Several studies have demonstrated that DOC is a significant component of fluvial carbon budgets (Pastor *et al.*, 2003; Worrall *et al.*, 2003b; Billett *et al.*, 2004) and have found that DOC concentrations increase as a result of climate changes and disturbance to peatlands (Evans *et al.*, 2005). However, the actual magnitude of aquatic OC losses from a catchment mainly depends on its land use and hydrological response (Grieve, 1984; Blodau, 2002; Worrall *et al.*, 2006; Dawson and Smith, 2007). This highlights the importance of quantifying organic carbon fluxes arising from landuse change in peatland catchments.

One estimate of global riverine flux of DOC is 170 x 10^9 g C yr^{-1} as reported by Harrison *et al.* (2005), and the total export of DOC by rivers of Great Britain varies from 0.62 to 1.68 Mt C yr^{-1}(Worrall and Burt, 2007). When compared to DOC, only limited data are available on POC and a global flux estimate of 197 x

10^9 g C yr^{-1} is provided by Beusen *et al.* (2005). In a study on UK rivers, Worrall *et al.* (2007c) have shown that, in general, they are DOC-dominated and POC flux is estimated to be 0.38 x 10^9 g C yr^{-1}. However, in a study on a degraded southern Pennines catchment in the UK, Pawson *et al.* (2008) reported a total fluvial carbon flux of 92 g C m^{-2} yr^{-1}, of which POC accounted for about 80%. Worrall *et al.* (2003b) reported a wide range of UK peatland DOC fluxes from 2 g C m^{-2} yr^{-1} up to 70 g C m^{-2} yr^{-1} in the most degraded peatland.

Various restoration studies on drain-blocking techniques have shown that DOC concentrations and fluxes to streamwater were reduced as a result of drain-blocking (Wallage *et al.*, 2006; Worrall *et al.*, 2007a; Armstrong *et al.*, 2010; Wilson *et al.*, 2011), and that the magnitude of the decrease is dependent upon the drain-spacing (Worrall *et al.*, 2007a). The reason for such decrease in DOC flux to streams could be due to reductions in water discharge past the drains, rather than a decrease in DOC concentration leaving the drains (Worrall *et al.*, 2007b). For example, in a study on drained peat catchments, Gibson *et al.* (2009) found high DOC concentrations mainly come from the water ponded in the drains and DOC fluxes are a function water yield from the catchment. They therefore concluded that drain blocking works by decreasing the runoff from the drain, hence reducing DOC flux, rather than by altering the production of DOC in the peat. However, Wallage *et al.* (2006) have shown that DOC production can be significantly reduced through drain blocking and water table recovery within five years. Similarly, in a study on a restoration project in northern England, Holden *et al.* (2007) demonstrated that drain blocking has an immediate impact in that it can rapidly reduce the particulate carbon (POC) losses from a peatland. In a re-wetting study on a cutover peatland in Québec, Waddington *et al.* (2008) found that within the first few years post-restoration, DOC export from the restored site was reduced to less than a half of that from the cutover site. Although various studies on different restoration methods

document the effects related to water table level, organic carbon exports and greenhouse gas emissions (Vasander *et al.*, 2003; Wallage *et al.*, 2006; Worrall *et al.*, 2007b; Anderson, 2010; Sieg *et al.*, 2010), relatively little published information is available on the influence of felling-to-waste restoration on OC exports.

Recent studies have identified climate change as one of the potential controlling factors that can influence production and export of DOC in stream waters (Evans *et al.*, 2002; Pastor *et al.*, 2003; Worrall *et al.*, 2004b; Evans *et al.*, 2005; Clark *et al.*, 2009; Arneth *et al.*, 2010). Hence, the influence of climatic variables on DOC concentrations has been extensively studied, with a primary focus on temperature (Freeman *et al.*, 2001), precipitation patterns (Tranvik and Jansson, 2002) and landuse change (Rowson *et al.*, 2010). Climate change models predict that higher temperatures are likely to occur over most of the UK over the next century (Hulme *et al.*, 2002). Therefore, variability in the severity and frequency of storm and drought events is also expected. Increase in temperature and hydrological changes (particularly, runoff) are likely to lead to changes in the quality and quantity of OC exports from terrestrial sources to rivers; such changes will have implications for acid-base chemistry and for the speciation and bioavailability of metals and nutrients.

The majority of organic carbon exports in headwaters occur during storm events (Grieve, 1994; Hinton *et al.*, 1997; Clark *et al.*, 2007) through processes such as leaching, flushing, and erosion depending on the hydrological connectivity (Inamdar *et al.*, 2004; Tetzlaff *et al.*, 2010) in the catchment and availability of removable OC (Worrall *et al.*, 2008; Evans *et al.*, 1999; Holden, 2006). During storm events, DOC concentrations vary dramatically depending on the hydrological flowpaths with dominant contributions from the top 15-20 cm of soil profile where the majority of labile carbon lies (Bishop *et al.*, 1990;

Brown *et al.*, 1999; Worrall *et al.*, 2003a; Billett *et al.*, 2006). Erosion studies on UK catchments that explain the controls on, and processes leading to, POC losses to streams have been undertaken on a wider scales of catchments (McHugh *et al.*, 2002; Evans and Warburton, 2005; Evans and Lindsay, 2010). These studies identified that in upland areas, erosion is highly variable and can be sensitive to disturbance due to landuse changes that may lead to removal of surface organic soils by runoff (Stott and Mount, 2004). The majority of POC losses are found associated with high rates of erosion and generally occur during storm events (Jung *et al.*, 2012), and due to this episodic nature it is often difficult to assess such processes over time (Evans and Warburton, 2005, 2007).

Any climatic change that significantly influences runoff will affect OC export to streams. In order to predict the effects of climate change on DOC removal, it is necessary to understand how the relationship between DOC and discharge changes with different hydrological conditions and within different catchments. Several studies have found significant positive correlations between DOC, POC and discharge (Grieve, 1984; Walling and Webb, 1985; Hope *et al.*, 1997a, 1997b; Dawson *et al.*, 2002). However, Clark *et al.* (2008) found a decrease in DOC with increased stream flow while Worrall *et al.* (2008) have noted both increases and decreases in DOC concentrations with stream discharges and concluded that the time between the storm events is the controlling factor for DOC flux/concentrations. Increase in DOC with discharge may be linked to the production and availability of DOC in the soil profile, whereas its decrease is generally due to exhaustion of DOC or dilution effect of storm waters. The relationship between POC and discharge is more complex than that of DOC and discharge, since POC requires a threshold energy within the stream to get transported (Lawler *et al.*, 1999). This highlights the significance of storm event sampling in order to understand the role of hydrological pathways in organic carbon transport.

Recently, there has been significant interest in investigating the mechanisms responsible for the DOC exports from a wide range of catchments (Hornberger *et al.*, 1994; Worrall *et al.*, 2002, 2006; Inamdar *et al.*, 2004; McClelland *et al.*, 2007; Wagner *et al.*, 2008) in order to understand the hydrological and chemical processes leading to DOC transport. For example, in upland forested catchments of the Colorado Rocky Mountains, Hornberger *et al.* (1994) found that the temporal variability in DOC concentrations was mainly due to the flushing of the near-surface soil DOC pool. In a similar study in the Trout Beck catchment, Worrall *et al.* (2002) identified that discharge from a peat system behaves like a three end-member system with between-event water being low in DOC and storm events characterised by two types of water (with varying DOC concentrations) depending on their relative resident times in the soil. In a forested catchment in Germany, Hangen *et al.* (2001) observed a delay in DOC concentrations with respect to peak hydrograph due to the time lag associated with the onset of stem flow and displacement of DOC-rich waters from the topsoil to the stream via macropores. Similarly, in a forested catchment in New York, Inamdar *et al.* (2004) ascribed the observed delay in DOC peak to the hydrological connectivity in the catchment. Given that soil structure is disturbed due to the felling of trees and installation of drain blocks, the DOC export and DOC flushing efficiency may well be increased.

In the Dyke catchment, a sub-catchment of River Halladale, the RSPB felled a forested plot (~430 ha) to waste between 2004 -2006 as a part of the LIFE peatland project, and blocked previously cut drains by installing plastic sheet and peat dams. Although there are no data available for this site prior to felling, this study can provide preliminary water chemistry and OC concentrations and fluxes 3-5 years post-restoration. Moreover, there is not much information available on the effects of felled to waste practices on stream water quality and how efficiently this practice can return a degraded peatland to its pristine state.

While a large-scale project to re-wet the Forsinard peatland areas in Caithness and Sutherland is underway by the RSPB (pers comm.), there is very little background data on the current state of these systems, which is required if substantial benefits of the re-wetting programmes are to be demonstrated and quantified. Insight into the water quality and functioning of these disturbed and near-pristine environments is essential for predicting peatland responses to future climate change and an understanding of these global carbon stores is essential for predicting the future changes in peatland carbon storage capacity. Therefore, this study is unique in a sense that it a) adopts an integrated approach to identify the drivers and controlling mechanisms for organic carbon transport within, and from, the catchment, b) investigates the effects of felling for restoration on streamwater quality in terms of metals, base cations and organic carbon, and c) it compares the fluxes and mechanisms between the intact, forested and felled-to-waste plots in the catchment. It is anticipated that the findings of this study will provide a scientific basis for the future restoration (felling-to-waste) works that the RSPB intend to carry out in the Dyke catchment, and could be used as a comparison site for other catchments with a similar setting. Ecosystem services, in particular the use of peatlands as terrestrial carbon storage sites, is of national and international interest (*e.g.* McInnes, 2007). Detailed datasets on OC exports and the percentage increase in OC storage gained from restoration projects, as well as greenhouse gas fluxes, need to be quantified in order to develop peatland carbon storage as useful ecosystem services.

1.3. Aims & Objectives of this study

This study is motivated by current research on the influence of climate, and landuse change on carbon export from peatlands. Although previously forested peatlands have been subjected to recent restoration schemes as possible

strategies for peatland regeneration, such as felled to waste and drain blocking, very little is known about the efficiency and influence of such a change on the mechanisms of DOC export from these catchments and the effect of landuse change on DOC and discharge relationships. Therefore, the main aims of this study are to: i) provide a comparison of DOC-discharge relationships for disturbed and undisturbed sub-catchments in the Dyke catchment of the Halladale River (in Caithness), ii) to establish the mechanisms involved in DOC transport and identify the influence of landuse changes on DOC transport, and iii) to quantify annual organic carbon exports from the catchment.

Specific objectives of this study include:

1. monitoring background levels of stream water chemistry and investigating the spatial and temporal variability in DOC concentrations for the three sub-catchments,
2. investigating flow related variability in stream chemistry during hydrological events, in order to assess the contribution of different runoff source areas to stream flow during those events,
3. establishing principal differences in DOC concentration ranges between undisturbed (near pristine) and disturbed (forested and felled to waste) sites in the catchment,
4. examining DOC relationships with discharge, and identifying the sources and major flowpaths of DOC in the catchment,
5. investigating possible export mechanisms and developing conceptual models of DOC export,
6. quantifying organic carbon exports in a nested approach (from each sub-catchment and from the whole River Dyke catchment), and assessing landuse change impacts on organic carbon loads.

1.4. Thesis Framework

This thesis is presented in nine chapters covering one or more relevant objectives in each one of them as follows:

Chapter 1 is an introduction to the research questions and outlines the aims, objectives, and deliverables of the project.

Chapter 2 is a review of organic carbon in terms of its definition, nature, sources, drivers and controlling factors affecting its delivery such as climate change, landuse, and hydrologic pathways. It also reviews the significance of the magnitude and frequency of storm events, and outlines existing organic carbon flux estimates from recent studies in British upland catchments.

Chapter 3 presents the details of the study catchments including location, catchment characteristics such as geology, soils, and hydrology. A brief background of the catchment and justification for the choice of sites are provided.

Chapter 4 describes the sampling strategies, monitoring periods, field and laboratory (sampling treatment and analysis) methods adopted in this study, and justification for the choice of methods.

Chapter 5 provides the analysis required for *Objective 1.* This chapter examines the spatial and temporal variability in water chemistry during hydrological events and low flows, in order to provide a baseline streamwater chemistry for individual sub-catchments.

Chapter 6 focuses on *Objective 2.* This chapter describes methods of data analysis and statistical techniques like factor analysis and end-member mixing, and attempts to understand the hydrological setting in the catchment by analysing storm events and associated water chemistry. The result of these analyses is identification of preferential flowpaths taken by water *en route* to stream and source areas of DOC.

Chapter 7 presents the findings of objectives 3, 4 and 5. *Objective 3* establishes the principal differences between aqueous DOC concentrations from

the different landuse treatment sites in the catchment and is a prerequisite for identifying the possible processes responsible for DOC release from these land managements. *Objective 4* assesses the spatial and temporal variability of DOC and discharge relationships for each landuse area and integrates results from the above objectives to understand the landuse change impacts on organic carbon exports. Therefore, *Objectives 3 & 4* determine whether the modifications in export mechanisms brought about by changes in landuse management practices, coupled with seasonal variations in DOC, can be explained by variability in flow; this assesses the suitability of using discharge to predict DOC concentrations exported from the catchment. Hydrological flow paths in peats vary with the water table depth in conjunction with antecedent moisture conditions and land use. Thereby, water table disturbance in the form of forestry or felled to waste practices could alter the pathways of water movement within and through the peat such that runoff production processes are modified and alternative sources of DOC are made accessible. Therefore, *Objective 5,* based on objectives 3 and 4, identifies the export mechanisms and finally, presents conceptual models explaining the evolution of DOC during storm events.

Chapter 8 focuses on *Objective 6* to quantify annual DOC and POC exports from the sub-catchments and up-scaling to the whole Dyke catchment, and presents the flux calculations, estimates and uncertainties. In this chapter, the fluxes between the sub-catchments and between 2010 and 2011 are compared, and effects of landuse changes on DOC fluxes are discussed.

Chapter 9 is a discussion of the major findings of this study, provides a synthesis of the outcomes of chapters 5, 6, 7 and 8, outlines limitations and suggests future research, and presents the main conclusions of the thesis.

Chapter 2
BACKGROUND

Peatlands represent a highly significant carbon stores and are generally assumed to serve as net C sinks (Charman, 2002). However, recent carbon budget estimations, including aquatic carbon losses, suggest that while some UK peatlands are acting as net carbon sinks (Worrall *et al.*, 2003c), others are carbon neutral (Billett *et al.*, 2004). Climate, geology, topography, land management practices and in-stream processes are identified as the primary controlling factors on carbon losses from catchment soils (Hope *et al.*, 1994; Dawson *et al.*, 2001a; Clark *et al.*, 2004; Soulsby *et al.*, 2006; Yoo *et al.*, 2006). Therefore, this chapter is intended to provide a review of the available literature on the significance, drivers and controlling processes, and fluxes of organic carbon (OC) in peat-dominated catchments.

2.1. Fluvial Carbon in peatlands

Carbon from peatlands is exported to fluvial environments in four main forms: as dissolved organic carbon (DOC), particulate organic carbon (POC), dissolved inorganic carbon (carbonates) and dissolved carbon dioxide (CO_2) (Worrall *et al.*, 2003c). Of all these forms, dissolved and particulate forms constitute an important linkage to global geochemical cycle and are the major forms of carbon being exported from upland catchments (Grieve, 1991; Hope *et al.*, 1997b). Recent studies have demonstrated that fluvial organic carbon is an important component of terrestrial C budgets from peat soils (Aitkenhead *et al.*, 1999; Billett *et al.*, 2004; Pawson *et al.*, 2008) and increasing trends of DOC fluxes in streamwaters have been reported (Worrall *et al.*, 2004b; Evans *et al.*, 2005a; de Wit *et al.*, 2007). Several studies have found that temporal variability in DOC and POC concentrations and fluxes is a function of hydrological variability and

seasonality (Grieve, 1991; Holden and Burt, 2002; Ågren *et al.*, 2008; Clark *et al.*, 2008; Dawson *et al.*, 2008).

2.2. Dissolved Organic Carbon (DOC)

Organic carbon in stream waters originates from natural organic soil or plant material, which consists of about 50% of organic carbon (Thurman, 1985). Dissolved organic carbon (DOC) present in peatland drainage waters is an essential component for its control on the microbial activities, acidity, absorption of light, metal ion mobility and toxicity (Limpens *et al.*, 2008). Presence of DOC in water can alter its colour and much of the colour in water is due to the presence of humic acids leached from plant and soil organic matter (Thurman, 1985). Hemond (1990) proposed that the origin of these dissolved humic substances depends strongly on the streamflow generation in the catchment and the areas with immediate connection to streams are the primary sources of DOC, and has since been confirmed by field measurements (Bishop *et al.*, 1994; Fölster, 2001; Smart *et al.*, 2001).

Peat soils are the principal source of dissolved organic carbon for fluvial systems. Therefore, soil-fluvial DOC relationship is crucial in estimating peatland carbon budgets and their linkages to the global carbon cycle. To further highlight the significance of DOC in the carbon cycle, the following sections will define DOC, and discuss the sources and controls of DOC concentration in stream waters.

2.2.1. Definition of DOC

Dissolved organic carbon (DOC) has been operationally defined as the fraction of organic carbon in water that passes through a 0.45 μm filter (Bourbonniere, 2009; McDonald *et al.*, 2004; Thurman, 1985). This definition however has not been strictly adhered to and studies have been using different

pore size filters. For example, studies have used 0.45 μm pore-size filters (Biron *et al.*, 1999; Worrall *et al.*, 2002), 0.7 μm filters (Hope *et al.*, 1994; Dawson *et al.*, 2004; Billett *et al.*, 2006; Buckingham *et al.*, 2008), and 1.2 μm filters (Dalva and Moore, 1991; Baker and Spencer, 2004).

Hope *et al.* (1997a) have used TOC and DOC concentrations interchangeably in their study of DOC export from 85 British rivers, as they found that the difference between TOC (unfiltered samples) and DOC (filtered samples) content in the samples was less than 5%. Similarly, (Dawson *et al.*, 2001b) have measured DOC on unfiltered samples taken from a Scottish headwater stream, as POC concentrations in the samples were low (0.2-0.8 mg/l). However, the operational definition of DOC has remained.

DOC comprises of a variety of molecules that range in size and structure from simple non-humic acids and sugars to complex humic substances. Humic substances are generally the dominant fraction in DOC, since non-humic substances tend to decompose relatively fast compared to humic substances (Schnitzer and Khan, 1972; Thurman, 1985). Humic substances account for about 50% of the DOC in surface waters and they can account for as much as 90% of DOC in dark coloured waters (Kronberg, 1999). These humic substances are mainly composed of humic acids that are dark brown to black in colour and soluble in alkaline solutions, but insoluble in acid below pH 2. Fulvic acids are soluble in both acidic and alkaline solutions, and are light yellow to yellow-brown in colour, while humins are insoluble in acid or alkaline solutions. Hence, much of the colour in water is due to the presence of humic substances (Thurman, 1985) which results in a strong association between DOC and colour or absorbance. A substantial amount of research involving organic carbon export from peatlands has relied upon the use of colour or absorbance as a proxy for the determination of DOC (Dobbs *et al.*, 1972; Moore, 1985; Worrall *et*

al., 2002, 2003b; Worrall and Burt, 2004; Moore and Clarkson, 2007). However, humic substances in DOC have been found to vary between 30 and 90%, which means that, in some cases, uncoloured non-humic compounds can make up to 70% of DOC (Wallage *et al.*, 2006) and would not be measured using a colour spectrometry method.

2.2.2. Significance of DOC

Dissolved organic carbon constitutes the largest pool of organic carbon in most aquatic ecosystems and is a vital energy source for biological, chemical and physical processes in these systems (Limpens *et al.*, 2008). Therefore, transport of DOC from the soils into the aquatic environments is essential for provision of energy for heterotrophs (Hader *et al.*, 1998). In these ecosystems, UV-B radiation breaks down high molecular weight DOC into simpler DOC molecules that are then available for uptake by bacterioplankton, and they in turn, re-mineralize the carbon for use by other organisms (Hader *et al.*, 1998). DOC also protects water organisms from excessive exposure to UV radiation. The rate of transfer of DOC from soils to stream waters is an important parameter to understand, as aquatic DOC can affect biological process directly through interfering with metabolic processes, and/or indirectly by altering the availability of nutrients and toxic metals. Excessive DOC may attenuate oxygen availability and can be a growth-limiting factor in the aquatic systems. DOC can buffer against acidification, but may also add acidity to waters (Hruska *et al.*, 1999). Presence of high concentrations of DOC can impart unpleasant colour to freshwater, treatment of which is found to be expensive for the water companies in the UK.

Over the past few decades, there has been increased concern about climate change and landuse change, and their impact on fluvial ecosystems. In many studies the primary focus is towards export of organic carbon and metals to

downstream ecosystems in response to changing environmental and hydrological conditions (Grieve, 1990a; Heal, 2001; Cummins and Farrell, 2003; Worrall *et al.*, 2003a; Waldron *et al.*, 2009). However, a significant amount of research has been done to model and conceptualize catchment characteristics, and to get an insight into catchment internal processes such as runoff generation, hydrological pathways and interactions between processes occurring within the soil profile (Evans *et al.*, 1999b; Soulsby *et al.*, 1998, 2006; Burt and Pinay, 2005; Tetzlaff *et al.*, 2010). They found that the spatial and temporal variability in the stream water chemistry is principally explained by hydrological processes and catchment characteristics. Thus, the following sections outline the sources, processes and factors that are responsible for production, mobilisation and export of DOC and POC, and discuss how the variability in flow under changing hydrological conditions and different catchment characteristics affect DOC dynamics in peatlands.

2.2.3. Sources of DOC

DOC in peatland soils is produced from the decomposition processes of plant material. In general, stream water receives DOC and POC from allochthonous (from the soils and plants of the surrounding catchment) and autochthonous (from within the aquatic system) sources. The allochthonous organic matter ranges in size from coarse particulate organic matter (>1mm) to dissolved organic matter (<0.45μm), for example decomposing plant litter, leaves, twigs, and roots (Meyer *et al.*, 1998). Autochthonous DOC is derived from the instream breakdown processes of algal and bacterial biomass and particulate organic matter (Bertilsson and Jones, 2003), but only a small fraction of DOC in surface waters is contributed from these sources. The majority of stream water DOC comes from allochthonous organic matter (Thurman, 1985; Aiken and Cotsaris, 1995) via subsurface flow (soil water), surface runoff,

groundwater, canopy drip and stem-flow (Qualls and Haines, 1991). However, as a water body enlarges in size, from stream to river to ocean, allochthonous sources decrease and autochthonous sources increase (Thurman, 1985).

Peatland soils are huge stores of organic carbon that are composed of living biomass (eg. micro-organisms, intact plant and animal tissues), residues of plant litter in the early stages of decomposition, and soil humus that can no longer be recognised as tissues (Brady and Weil, 1999). Carbon from these organic soils is readily available to reach the streams via a range of hydrological pathways, thus making the soils a primary source of DOC. For example, Dillon and Molot (1997) found a good correlation between DOC export and the percentage of catchment area with peat cover (Aitkenhead *et al.*, 1999), suggesting that stream DOC is primarily derived from peats rather than from mineral soils. Similarly, Easthouse *et al.* (1992) have noted that the concentrations of DOC were relatively low in catchments dominated by mineral soils, or in the mineral horizons of any given catchment. Many studies have shown that soil in the surrounding catchment is the largest potential source of dissolved organic carbon (Aitkenhead *et al.*, 1999; Kalbitz *et al.*, 2000; Billett *et al.*, 2006) and the concentrations of DOC vary depending on the soil type. Production and transportation of DOC in peats are mainly controlled by the biological and chemical processes that release DOC, the retention processes (microbial utilization and sorption), the hydrological pathways and resident times (Charman, 2002). As the hydraulic conductivity in peatlands decreases rapidly with depth (Fraser *et al.*, 2001), majority of DOC is mobilized and transported from the upper peat layers (Moore, 2003). For example, Billett *et al.* (2007), based on the isotopic evidence found that the age of DOC released from UK peatlands is consistently young (modern to 202 years BP), and mainly comes from the upper layers of peat (Clark *et al.*, 2008). Similarly, Evans *et al.*

(2007) have used ^{14}C dating and demonstrated that DOC lost from a peat profile was young, from relatively fresh material, rather than humified peat.

Several studies have reported that DOC concentrations decrease with increasing depths in peat systems (McDowell and Likens, 1988; Moore, 1989; Grieve, 1990b, 1990c; Hiederer, 2009). This decrease in DOC with depth is initially due to microbial metabolism (Allan and Castillo, 2007), but in the mineral horizons such as B, DOC is absorbed to metals oxides and hydroxides of iron (Fe) and aluminium (Al) (McDowell and Wood, 1984; Moore *et al.*, 1992). Therefore, soil type within a catchment controls the amount of DOC that is available for export, and in catchments with organic-rich soils DOC is readily available for export than in catchments with a larger percentage of mineral soils. However, hydrologic connectivity within the catchment and the access to the soil C pool dictates the concentrations of DOC removed in solution (Billett *et al.*, 2006).

2.3. Particulate Organic Carbon (POC)

Particulate organic carbon is the fraction of carbon in the sediment retained on a filter with pore sizes between 0.45 and 1.0 μm (Dawson *et al.*, 2002; Thurman, 1985). High intense storm events and wet antecedent conditions prior to heavy rainfall may lead to high rates of erosion, hence increased POC losses (SNIFFER Report, 2011). In a study on a blanket peat catchment in the north Pennines, Evans *et al.* (2006) have demonstrated that POC losses are associated with erosion and account for the majority of carbon losses from the system, and they have shown that the catchment is close to carbon neutral. In bog systems, it is likely that majority of POC to streams comes from the macropores in peat (e.g. pipes) depending on the connectivity to stream network (Holden, 2005). Given the increasing interest in landuse change studies recently, in a study on drained catchments, Holden (2006), based on the log

linear relationship between POC and the age of drainage, found that POC losses increased with the age of drainage. Low density eroded peat is the major source of POC in upland peat systems which is largely transported as wash load and deposited where the flow is very weak (Thurman, 1985; Charman, 2002). In some cases, POC may breakdown by mechanical comminution of stream biota action to produce DOC (Evans and Warburton, 2001; Charman, 2002).

Flow extremes during storm events increase water erosion potential and POC exports which may provide a positive feedback to climate change (Holden and Burt, 2002; Evans and Warburton, 2005). Particulate organic carbon, in general, is not measured directly; hence, the majority of the research on POC is based on sediment analysis and literature assuming that POC accounts for about 50% of the suspended organic load (*e.g.* Hope *et al.*, 1997; Worrall *et al.*, 2003; Pawson *et al.*, 2008). The factors controlling POC transport from peat soils are relatively less investigated than for DOC.

Most studies investigating the C export of organic carbon by streams only quantify the DOC flux, which is the dominant component of the total organic flux (Dawson *et al.*, 2002), hence may underestimate the aquatic C flux. Fluxes of POC from northern peatlands are estimated to range from 2 to 40 g m^{-2} yr^{-1} (Dawson *et al.*, 2002; Evans and Warburton, 2005). Moreover, inclusion of POC fluxes has been proved to be important as it increased the C flux estimates significantly (Hope *et al.*, 2001; Dawson *et al.*, 2002; Billett *et al.*, 2004). POC fluxes from disturbed catchments may sometimes vary as much as 80% (Pawson *et al.*, 2008) or considerably greater than that from undisturbed catchments, hence must not be ignored while investigating the OC budgets for such catchments. Worrall *et al.* (2007a) have noted that there appears to be a

positive trend in POC with time, which could be due to increases in river discharge (Werritty, 2002).

2.4. Organic Carbon fluxes

One estimate of average global riverine flux, as reported by Hope *et al.* (1994) vary between 1 and 10 x 10^{11} kg C yr^{-1}, and another estimate of 170 x 10^{9} g C yr^{-1} was given by Harrison *et al.* (2005). The total export of DOC by rivers of Great Britain has been estimated to vary between 0.62 and 1.68 Mt C yr^{-1} (Worrall and Burt, 2007a). When compared to DOC, only a limited data is available on POC with a global flux estimate of 197 x 10^{9} g C yr^{-1} as given by Beusen *et al.* (2005). Fluxes of organic carbon in UK rivers have been reported as 0.7 x 10^{12} g DOC yr^{-1} and 0.2 x 10^{12} g POC yr^{-1} by Hope *et al.* (1997b); these values may underestimate true exports since they do not include data from high flow events when the majority amounts of organic carbon is exported (Hinton *et al.*, 1997). In another study on UK rivers, Worrall *et al.* (2007b) have shown that UK rivers are, in general, DOC-dominated (Baker *et al.*, 2008) and an average POC flux is estimated to be 0.38 x 10^{9} g C yr^{-1}. Similarly, in a study on catchments in NE Scotland and Mid-Wales, Dawson *et al.* (2002) found that while DOC fluxes at the NE Scotland and Mid-wales sites are 169 kg C ha^{-1} yr^{-1} (88.4% of TOC) and 83.5 kg C ha^{-1} yr^{-1} (69% of TOC) respectively, POC accounted for about 10% and 22.6% at the two sites respectively. However, in a similar study on a degraded southern Pennines catchment in the UK, Pawson *et al.* (2008) reported a total fluvial carbon flux of 92 g C m^{-2} yr^{-1}, of which POC accounted for about 80%.

2.5. Factors influencing DOC

2.5.1. Climate change and DOC

Climate models' predictions suggest greatest warming at high latitudes and climatic extremes may be the trend in the 21st century (Beven, 1993; Karl and Trenberth, 2003; Meehl *et al.*, 2006; Wilby *et al.*, 2008), hence the high latitudes occupied by peatlands are expected to witness the greatest amount of warming. In addition to increasing temperatures, climate change could also affect the precipitation patterns and discharge which indirectly influence the depth to watertable in peat systems (Pastor *et al.*, 2003). Such changes in climate could may have a direct impact on production and transport of DOC to downstream ecosystems (Tranvik and Jansson, 2002; Worrall and Burt, 2005; Bridgham *et al.*, 2008; Clark *et al.*, 2009). An increasing trend in riverine DOC concentrations has been reported (McCartney *et al.*, 2003; Worrall *et al.*, 2004a; Evans *et al.*, 2005b; Worrall and Burt, 2007b) and has been a primary focus of research in recent times.

Field and experimental studies have shown that the production of DOC within a soil profile is driven principally by changes in temperature (Andersson and Nilsson, 2001; Neff and Hooper, 2002) and increase in temperature increases the rate of DOC production (Pastor *et al.*, 2003). Cole *et al.* (2002) noted that warming of the soil increased the abundance of enchytraeid worms and thus increased soil DOC concentrations. The rate of decomposition by soil biota may increase with lower water table levels. As the watertable drops, more of the peat profile is exposed to decomposition, thus increasing the production of DOC, particularly during droughts. DOC produced during drier periods is stored within peats until it is removed in solution or exported to the atmosphere through microbial respiration as CO_2 and CH_4 (Pastor *et al.*, 2003).

Freeman *et al.* (2001) have proposed that increase in temperature increases the activity of the enzyme phenol oxidase. The anaerobic conditions within a peat system prevent phenol oxidase from degrading phenolic compounds. These phenolic compounds accumulate and subsequently inhibit the activity of hydrolytic enzymes that decompose the peat. Increased activity of this enzyme would quicken the decomposition of the peat and thus increase the release of DOC and CO_2. This study has, however, been criticized by Tranvik and Jansson (2002) for not accounting for the influence of varied precipitation patterns on the measured DOC. This criticism has been defended by Evans *et al.* (2002), who argued that DOC export is a two-step process: DOC is first produced in the soil and then transported to streams; therefore, over the long-term the effect of discharge on DOC concentrations will be limited by the supply of DOC.

In Scotland, climate change scenarios have predicted both increases in annual precipitation and the intensity of precipitation (Hulme *et al.*, 2002). It has been widely accepted that the highest DOC concentrations are generally associated with high rainfall events which can account for a substantial amount of the annual carbon exports since a significant relationship exists between DOC concentrations and stream discharge (Grieve, 1984; Hope *et al.*, 1997a; Worrall *et al.*, 2002). Further, greater precipitation intensity produces larger storm peaks and frequent intense storms result in high flow hydrographs, which implies higher DOC exports. Schiff *et al.*, (1998) have observed that approximately 50% of the total DOC export occurs during the upper 10% of the flow values, and suggested that many sampling programmes thus underestimate the total DOC export as they may miss at least some of the high flow events. Although discharge is directly related to delivery of DOC to streams, higher discharges may not always necessarily result in higher DOC concentrations, rather it depends on the availability of DOC (Evans *et al.*, 2002) and time since the last storm event (Worrall *et al.*, 2002). That is, during a runoff

event discharge of a given volume may not export the same amount of DOC every time, due to depletion or exhaustion of available DOC. This signifies that, monitoring of DOC concentrations during hydrologic events of different magnitude is essential in order to develop an annual organic carbon budget for any catchment.

2.5.2. Landuse

Landuse changes can have dramatic effects on peatland hydrology that can be associated with drastic changes in DOC and metal mobility. In the UK, peatlands with high organic soil content have been drained to lower the water table for forest plantation or for grazing purposes which may cause additional carbon production (Freeman *et al.*, 2001), turning them into potential DOC sources (Hargreaves *et al.*, 2003). Over a few decades in Scotland, 25% of Caithness and Sutherland peatlands have been seriously affected by afforestation (Ratcliffe and Oswald, 1988). Narrowly spaced drains and ditches dug for forestry lowered the water table resulting in peat subsidence (Anderson *et al.*, 2000) and induced increase in hydraulic conductivity in the upper peat layers. Consequently, further losses of moisture from peat layers incurred by plant respiration increases the zone of aeration in the soil, thereby increasing the microbial activity and thus more DOC production (Freeman *et al.*, 2001). DOC concentrations in runoff from forested sites may further increase due to the leachate from leaf litter, canopy drip and underlying humus (McDowell and Likens, 1988). Typically, streams draining forest catchments have high DOC concentrations than those draining open peatland catchments (Aitkenhead *et al.*, 1999). This is because the acidity in forested catchments is higher compared to that of open peatlands (Grieve, 1990a) and acidity influences the solubility of DOC. Similarly, POC production and export have been reported to be

significantly greater from drained peat catchments than intact peatlands (Holden, 2006; Holden *et al.*, 2007; Ramchunder *et al.*, 2009).

Recently introduced restoration techniques like drain blocking, felling to waste, and furrow damming have been adopted worldwide to regenerate peatlands in order to increase carbon storage. Cummins and Farrell, (2003) in a study on forested catchments noted that disturbance caused by felling of trees distinctly increased DOC exports immediately following felling. However, Worrall and Burt, (2007a) demonstrated that drain blocking to reduce DOC loss had limited effect on DOC concentrations in the short-term (one year), whereas Wallage *et al.* (2006) have shown that DOC production can be significantly reduced through drain blocking and water table recovery in five years. Further, Holden *et al.* (2007) have noted that drain blocking has an immediate impact in reducing the particulate carbon (POC) losses from a peatland. Re-vegetation of drains/gullies reduces POC losses (Evans and Warburton, 2005) as rapid runoff is reduced. Felling of the trees and drain blocking for restoration of peats causes the watertable to rise, but the watertable tends to be much more sensitive than in intact peatlands, at least for a short term, because of changes in soil structure (Moffat *et al.*, 2011). In the Dyke catchment, realizing the importance of these natural carbon stores, the RSPB have undertaken peatland restoration by felling of forestry to waste and blocking the previously cut drains, as part of LIFE EU Peatlands Project. These tree-felling operations were mostly handled manually to minimize soil and sediment disturbance that would otherwise arise from the use of heavy machinery.

2.5.3. Catchment characteristics

Although hydrological processes explain the temporal variability in streamwater chemistry, catchment characteristics such as catchment physiography, geology, and landuse influence the spatial variability in stream

water quality. Numerous studies examining the controls on aqueous DOC concentrations and fluxes from peatlands have shown that DOC was influenced by catchment size and slope, percentage peatland cover, precipitation and vegetation (Eckhardt and Moore, 1990; Dalva and Moore, 1991; Grieve, 1994). Fluxes of carbon in the form of DOC from peat soils have been reported as ranging up to 85 mg C $km^{-2}yr^{-1}$ (Dawson and Smith, 2007). Of these, the highest values were reported for the smallest catchments, where the proportion of peat to non-peat sources is very high and in-stream processes have had little opportunity to modify DOC concentrations (Dawson *et al.*, 2001a). In a study on forested catchments in the Precambrian Shield, central Ontario, 78% of the variance in the export of DOC was explained by the proportion of land covered by peatlands (Dillon and Molot, 1997). Similarly Aitkenhead *et al.* (1999) have found a strong relationship between DOC concentration and catchment soil-carbon pool. In another study on 68 small boreal forest catchments in western central Sweden, Andersson and Nyberg (2008) have shown that, the topography of a catchment better explains the variation in DOC flux, rather than the percentage of wetland area. In small upland headwater catchments, Hope *et al.* (1997b) have found that peatland cover was the single most important predictor of variability in DOC exports between streams; moreover, the differences in soil organic C pool were found to explain 91% of the variance in annual DOC fluxes. Hence, it can be highlighted that soils are the most useful catchment characteristic in explaining variations in DOC fluxes. However, the type of soil and its development in a catchment is a function of altitude, geology, mean annual temperature, and slope of a catchment (Jenny, 1994; Lundström *et al.*, 2000). Thus, topography, geology and slope of the catchment may also impact organic carbon in peatlands. In a study on upland soil DOC in western Scotland, Grieve and Marsden (2001) have shown that total organic carbon (TOC) concentrations were correlated negatively with slope angle and

positively with altitude. Underlying geology of a catchment determines weathering and soil development processes in the catchment thereby indirectly effecting the physical and chemical interactions within the soil (Lundström *et al.*, 2000). For example, Nelson *et al.* (1992) in a study on two adjacent forested catchments found that the release of DOC concentrations to streamwater decreased in Cretaceous soils due to much higher absorption capacity than that in Tertiary soils with low absorption capacity. Minerals are known to influence the quality of DOM/DOC in stream water through sorption in soils, which results in removal or decrease in relative abundance of certain components of organic matter (Mosher *et al.*, 2010). Hence, bedrock weathering in a catchment may indirectly affect DOC, base cation and metal ion concentrations in stream waters draining the catchment. Water chemistry in base-poor environments such as bogs that are underlain by rocks like granite or sandstone possess lower pH and lower exchangeable base cation concentrations compared to sites dominated by base-rich bedrock (Billett and Cresser, 1996). Romkens *et al.*, (1996) demonstrated in their sorption studies on DOC that DOC concentration depends on the presence of Ca, such that increasing Ca content produced decreasing DOC because of sorption and precipitation processes. Their results indicated that a large part of the available DOC is in a Ca form at near neutral pH values. Thus, it is clear that the base cation availability in the bedrock controls the buffering capacity of the overlying soils and hence the acidity of the drainage water which in turn controls the concentrations of DOC.

2.5.4. Hydrologic pathways:

Hydrological pathways or routes that water follows to reach a stream channel have a strong control on the concentrations of organic carbon. In the UK, upland streams are highly flashy in nature, for example, discharge peaks rapidly in response to heavy storm events and falls rapidly once the event

ceases. Consequently, dramatic changes in water chemistry are generally associated with such periods of high discharges (Cresser and Edwards, 1987; Abesser *et al.*, 2006b, 2006a). Distinct chemical changes are associated by an increase in DOC, and metals like Al, Fe and Mn increase, while pH, conductivity and base cation concentrations decrease (Abesser *et al.*, 2006a; Abesser and Robinson, 2010). These changes are due primarily to changes in hydrological pathways during storm events, for example, despite low DOC concentrations in rainwater (Neal *et al.*, 2005), water draining laterally through the organic rich layers of peat tends to be high in DOC concentrations. Water moves laterally through the upper soil horizons either as unsaturated flow or more typically as shallow perched saturated flow above the main groundwater level (Ward and Robinson, 2000). This flow occurs when the lateral conductivity in the upper horizons of the soil profile is considerably greater than the overall vertical conductivity of the soil profile. Therefore, initial DOC concentrations are high during a storm event as the event water raises the watertable, and the water moves laterally through organic rich upper soil horizons. However, during a prolonged precipitation, dilution could result in lower DOC concentrations. Hence, flowpaths are a function of the intensity and length of the rainfall event, and the time since the previous rainfall (Worrall *et al.*, 2002). This suggests that the rainfall-runoff response time of the soil-stream system and the rainfall event frequency influence the temporal variability in the relationship between precipitation and DOC concentration.

At low flows, stream water mainly comes from lower mineral soils and ground water, which is of relatively deep origin and usually long residence times. As the water moves through deeper horizons, the processes such as mineral weathering, cation exchange, decomposition of organic matter, adsorption, oxidation and reduction alter the water chemistry producing less acidic baseflow chemistry, which is rich in base cations such as Ca, Mg and Si,

and depleted in metal ions such as Al, Fe, Mn (*e.g*. Neal *et al.*, 1997). During intense storm events, runoff generation processes and hydrological pathways shift from deeper base-flows to shallow subsurface and surface flows, which increase the stream discharges. At such flows, the runoff is predominantly through upper organic and organo-mineral soil horizons thereby water chemistry tends to be more organic-rich. As the hydrological pathways vary at different flows, a variety of chemical patterns each with a distinct set of chemistry is observed.

In general, during storm events runoff takes three basic flowpaths for stream flow generation: overland flow, shallow sub-surface flow and deep sub-surface or ground water flow. Overland flow is a surface flow that occurs in two ways, either as Hortonion overland flow where the rainfall intensity exceeds the rate of infiltration, and as infiltration excess or saturated overland flow (Ward and Robinson, 2000). Jenkins *et al.* (1994) opined that Hortonian overland flow is unlikely to be an important hydrological pathway in the case of upland catchments, except in arid areas, alternatively, saturation-excess overland flow, which occurs when the soil infiltration capacity is nearly zero resulting in water moving down slope, is commonly seen in uplands (Becker and McDonnell, 1998). However, Burt *et al.*, (1990) suggested that blanket peat catchments in the UK produce significant 'Hortonian' infiltration-excess overland flow since infiltration rates into peat appeared to be low. Holden and Burt (2002) in an experimental study have shown that these low infiltration rates were a result of surface saturation of the peat and found that saturation-excess overland flow can develop even during very low-intensity rainfall. Shallow water table areas adjacent to the stream channels and subsequently the lower valley slopes and hill slopes are the major sources for such flows (Evans *et al.*, 1999a; Ward and Robinson, 2000). As a hydrological event progresses, saturated areas expand and more areas in the catchment become sources of

runoff; in contrast, as the event ceases, the sources areas shrink. This is the basis for the popular 'variable source area concept' (Hewlett and Hibbert, 1967). When the overall vertical conductivity is overcome by the lateral conductivity, horizontal flow through soil layers as 'sub-surface flow' occurs. This lateral movement of water can occur through upper soil horizons or at shallow perched water tables above groundwater (Ward and Robinson, 2000). However, the hydraulic conductivity of peat is unlikely to be uniform in all directions (Surridge *et al.*, 2005), for example, there exists some perched conditions where sub-surface flow may break back through to the surface, termed as 'return flow'. At low flow conditions, the movement of water is mainly through deeper mineral horizons as 'groundwater flow'. Another significant subsurface flow path in upland areas is pipe-flow and macro-pore flow (Beven and Germann, 1982; Holden *et al.*, 2001). In forest soils, water moves rapidly through macropores or pipes that include old root channels, cracks or animal burrows (Holden and Burt, 2003). Movement through these macropores and pipes is important in that they are the major source of stream acidity even under baseflow conditions, and sources of DOC and Al under high flows (Jones, 2004). Consequently, stream water chemistry reflects the hydrological pathways followed by the water before reaching the stream channel. A combination of one or more of the above pathways can explain the majority of the variability in stream water chemistry. For example, in a study on radiocarbon ages of DOC exported from peatlands, Schiff *et al.* (1998) have found that almost all DOC in stream waters is produced in the uppermost layers of peat (Billett *et al.*, 2006), however groundwater is more likely to contain older carbon indicating that the soil water component is the major controlling factor.

There has been increasing interest in investigating the mechanisms responsible for the DOC exports from a wide range of catchments (Hornberger *et al.*, 1994; Worrall *et al.*, 2002, 2006; Inamdar *et al.*, 2004; McClelland *et al.*, 2007;

Wagner *et al.*, 2008) in order to understand the episodic response of DOC to varying hydrological conditions, and the chemical processes leading to DOC transport. In upland forested catchments of the Colorado Rocky Mountains, Hornberger *et al.* (1994) found that the temporal variability in DOC concentrations was mainly due to the flushing of the near-surface soil DOC pool. In a similar study in the Trout Beck catchment, Worrall *et al.* (2002) identified that discharge from a peat system behaves like a three end-member system with between-event water being low in DOC and storm events characterised by two types of water (with varying DOC concentrations) depending on their relative resident times in the soil. Similarly, in a forested catchment in Germany, Hangen *et al.* (2001) observed a delay in DOC concentrations with respect to peak hydrograph due to the time lag associated with the onset of streamflow and displacement of DOC-rich waters from the topsoil to the stream via macropores. In a study on a forested catchment in New York, Inamdar *et al.* (2004) ascribed the observed delay in DOC peak to the hydrological connectivity in the catchment and developed conceptual models to explain DOC evolution during storm events.

2.6. DOC and metal ion interaction

Organic complexation plays an important role in metal export from upland peats, especially Al, Mn and Fe, and their concentrations in stream waters often increase at higher discharges where DOC increases (Reid *et al.*, 1981). Humic and fulvic acids of DOC in soils provide ligands for Al, Fe and Mn by forming highly stable organo-metal complexes known as chelates. These processes remove metals from soils into solution and aid their mobility within the soil profile (Livens, 1991). However, since DOC decreases with depth (Tate and Meyer, 1983), these processes of metal complexation become predominant in the upper more organic-rich horizons of peats soils. Therefore, dissolved

organic matter controls the chemistry, solubility and transport of Fe, Al, Mn and trace metals in the upper horizons of peat soils and their export to streams (Hughes *et al.*, 1990; Romkens *et al.*, 1996; Tipping *et al.*, 2002).

Decomposition of organic matter in peats soils and microbial metabolism processes alter the redox potential and pH of the soil. DOC sorption in soil profiles is strongly related to pH, for example, decrease in soil pH leads to a decrease in the net negative surface charge and hence more ligands are removed from solution (Romkens *et al.*, 1996). Equally, pH of the soil solution is an important factor in controlling mobilisation and export of metals in that the solubility of metal oxides increases under acidic conditions (Cresser *et al.*, 1993). DOC production peaks in summer months due to increase in temperatures, and DOC accumulated during summer is flushed out during autumn rainfall events (Worrall *et al.*, 2002). Despite higher rainfall and lower evapotranspiration rates over winter months, DOC fluxes are limited by reduced temperature-dependent microbial activity (Grieve, 1984). Similarly, metal exports show a clear seasonality, for example, maximum metal loadings often occur in late summer/early autumn storm events (Neal *et al.*, 1997; Heal, 2001). Thus, it is clear that DOC and metal mobilisation and transport are closely linked.

From the above discussion, it has been noted that a range of factors could account for the spatial and temporal variability in DOC concentration in stream waters. In the environmental and climate change context, the processes responsible for variability in stream water DOC need to be understood in order to predict the responses of peatlands to future climate change. Moreover, increases in DOC exports would have severe implications, including a reduction in the global carbon store, changes in productivity downstream, increase in metal toxicity and watercolour, and would influence aquatic ecosystems. Hence, it is also important to understand DOC dynamics due to

land use changes to plan and execute future land-management strategies that reduce carbon exports from peatlands.

DOC production within peats can occur in aerobic and anaerobic decomposition of organic matter, while aerobic pathway favours DOC mineralization to CO_2, anaerobic pathway favours DOC transformation to CH_4 (Blodau, 2002). Therefore, although it is understood that increased water levels as a result of restoration reduces erosion and fluvial carbon losses (Wilson *et al.*, 2011), it would be interesting to see how this may affect the production and release of CO_2 and methane (CH_4), which would be accounted for when calculating total carbon budget for a catchment.

Chapter 3
THE RIVER DYKE CATCHMENT

3.1. Introduction

The Halladale river is a privately owned salmon fishing river managed by the Strath Halladale Partnership, and is located within the Caithness Flow Country blanket bog system of northern Scotland, the UK's largest (~ 4000 km^2) terrestrial carbon store *(Figure 3.1)*. The Halladale River drains the hills to the southeast of Forsinard, and flows northwards into the Pentland Firth at Melvich bay; this 29 km long river drains an area of about 267 km^2. The Dyke river, which is ~ 13 km long, is the major tributary of the Halladale converging with the main stem of the River Halladale from the west, just south of Trantlemore, which is about 13 km south to the Pentland Firth *(Figure 3.1)*.

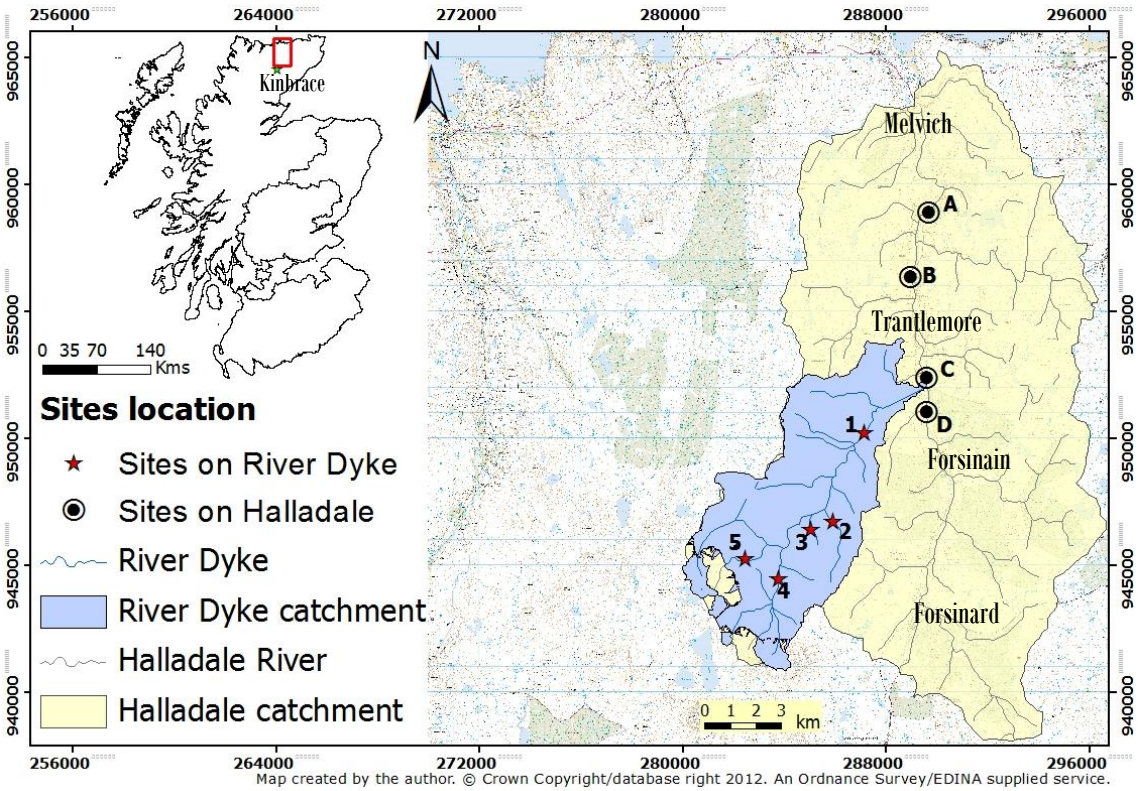


Figure 3.1: Location of study area in Scotland, and the Dyke and Halladale catchments.

Based on the 1:10,000 digital elevation model of the area (data derived from Edina Digimap), the Dyke river drains an area of approximately 54 km^2 with elevations ranging between 20m above mean sea level (AMSL) near the confluence with the Halladale river in the northeast, to 574m AMSL in the southern part of the catchment *(Figure 3.2a).*

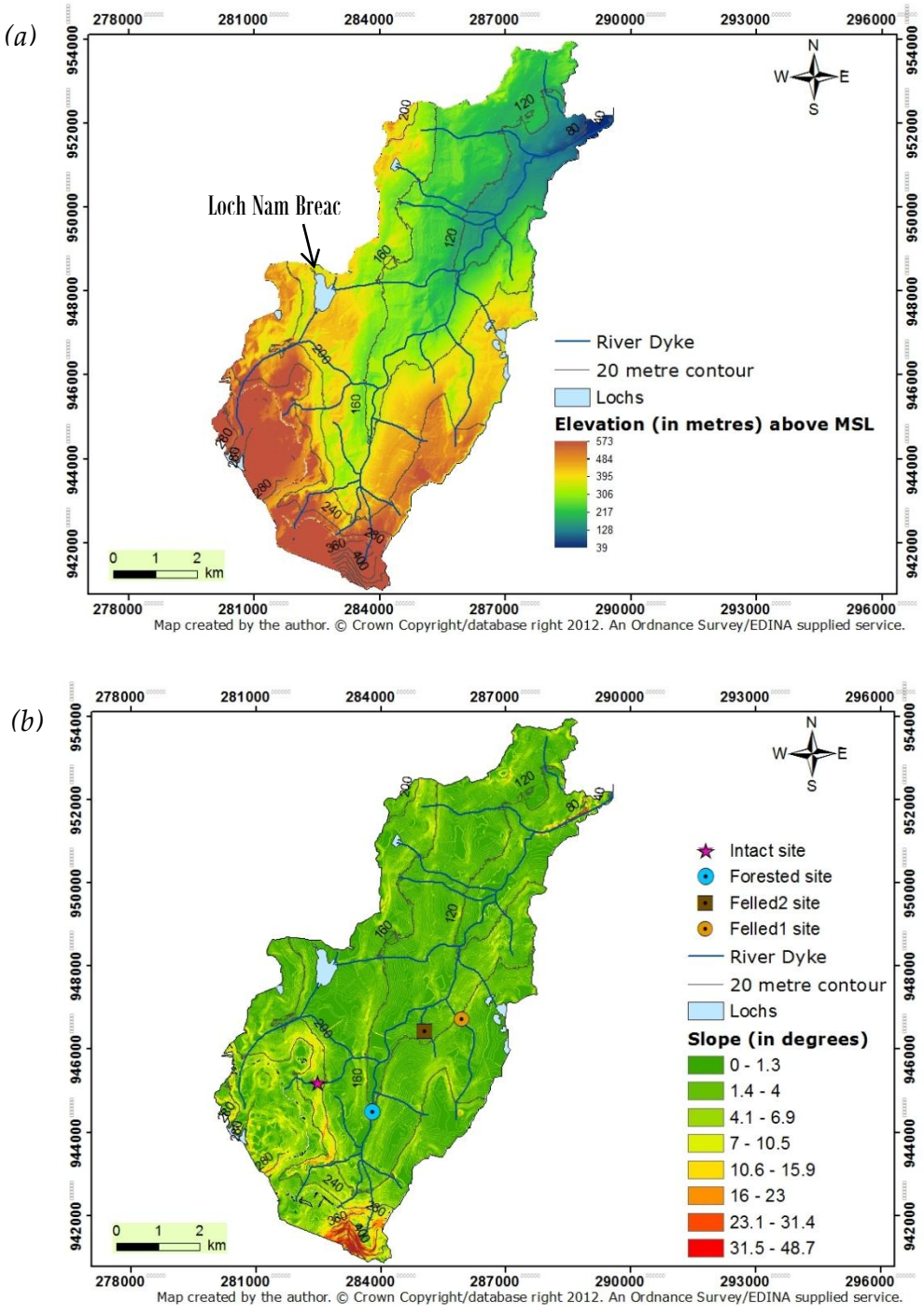


Figure 3.2: Map showing (a) elevation (in metres above mean sea level) (b) slope (in degrees) and lochs in the Dyke catchment.

3.2. Climate and Hydrology

The Scottish Environment Protection Agency operates a rain gauge station at Forsinain (NC 90632 48485) in the River Halladale catchment. From 1976 - 2005, the average annual rainfall in the Halladale catchment area is 1147mm, with a mean annual runoff of 776 mm and a mean discharge of 5.02 m^3s^{-1} (Marsh and Hannaford, 2008). The latest set of 30-year averages for 1971-2000 estimate the mean annual minimum and maximum temperatures as 3.1^{0}C and 11.1 ^{0}C, respectively (Met Office, 2012) from the nearest Met Office weather station in Kinbrace, south of Forsinard *(Figure 3.1)*. Relative to the Dyke catchment study sites in this project, the Forsinain rain gauge is ~ 4 km to the northeast, and the Kinbrace weather station is ~ 13 km to the south *(Figure 3.1)*.

The mean annual discharge estimated for the Dyke catchment (up-scaled from the discharge measured at one of the gauged sites) for the year 2010 is about 3.4 ± 0.1 m^3s^{-1}. The headwaters of the Dyke river comprise of lochs and pools of various sizes and these represent 1.2% (0.62 km^2) of the surface area of the catchment (see *Figure 3.2*). One of the lochs (Loch nam Breac) provides water to the Dyke river during dry months through a stream called Allt loc nam Breac and this converges with the Dyke river downstream of the main sites monitored in this project. The loch has a sluice system, which is operated by Strath Halladale Partnership to maintain an artificial flow regime during low flows. The Dyke river converges with the main stem of Halladale River at about 1.3 km south of Trantlemore *(Figure 3.1 & Figure 3.12b)*, and contributes nearly 50% of the total discharge to the Halladale. , It therefore has a major influence on the water chemistry of the Halladale River (Roberts, 2008).

Movement of water through peat

An undisturbed peat bog system comprises an upper 'active peat layer with relatively high hydraulic conductivity and fluctuating water table, and a 'less active' or 'inert' lower layer which is a permanently saturated main body of

peat (Ivanov, 1981). The upper (periodically aerated) layer is 'acrotelm' that generally varies between 0 - 50 cm in thickness, and the lower anaerobic layer is 'catotelm' which extends below acrotelm down to the mineral soil zone (Ingram and Bragg, 1984; Holden and Burt, 2003a, 2003b; Holden, 2005). In the present study water moving through acrotelm is termed as 'shallow soilwater', that moving through catotelm is considered as 'deep soilwater' whereas 'groundwater' is essentially the water interacting with the mineral soils (weathering zone) near the bedrock.

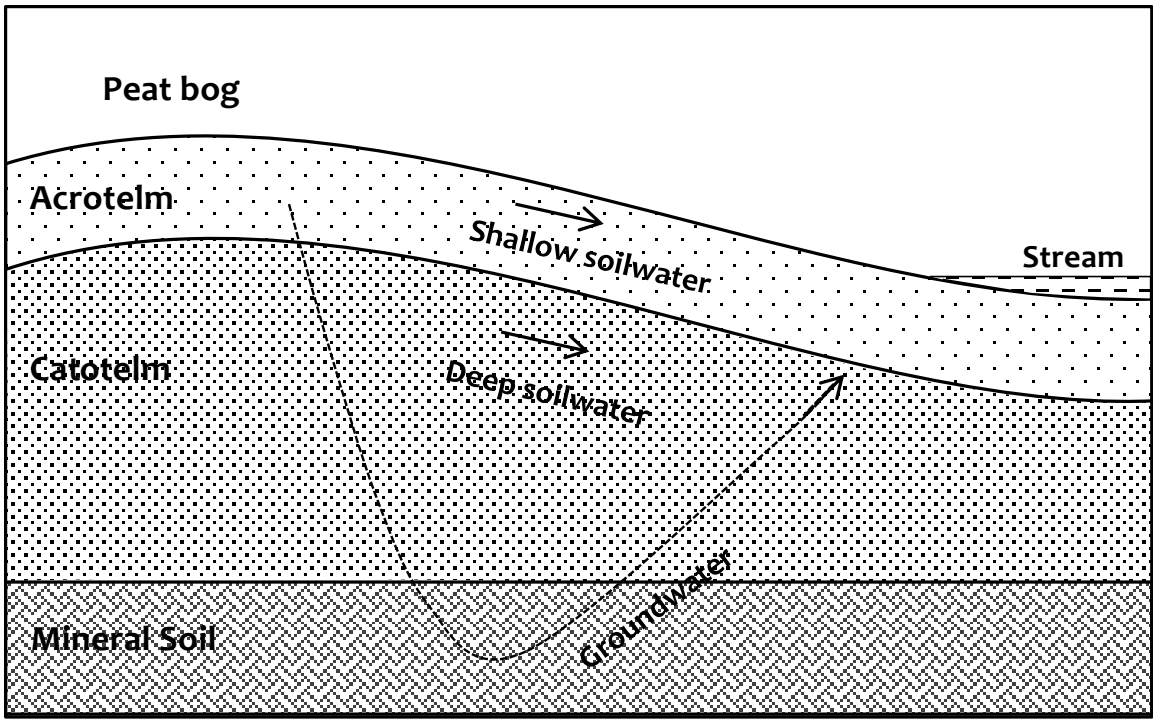


Figure 3.3: Diagram showing cross-section of, and water movement in an undisturbed peat bog.

3.3. Geology, Geomorphology and Soils

The extensive areas of blanket bog in the Flow country are spread over the Old Red Sandstone of Caithness, the large granitic intrusion along the Caithness-Sutherland boundary and about half of the area of Moine granulites and schists in Sutherland (Lindsay *et al.*, 1988). The Moine Supergroup are a thick succession of metamorphosed sedimentary rocks, mainly psammites,

pelites and semi-pelites, which cover the majority of the Northern Highlands of Scotland (Howarth and Leake, 2002; Trewin, 2002).

The Moine metasediments, deposited 1.1 billion years ago as sandstones and shales on a 'Lewisian' metamorphic basement, dominate the underlying bedrock of the River Dyke catchment (Trewin, 1993). These metasediments were subjected to metamorphism, migmatisation and several phases of deformation, culminating in the final the Moine thrust phase around 425 Ma (Trewin, 2002). Migmatitic psammite, pelite, and semipelite, are the dominant rock types in the River Dyke catchment *(Figure 3.4a)*. The rocks of the Moine Series and its intrusions are hard and resistant to weathering, as they are mostly non-calcareous and acidic, hence they give rise to base-deficient soils (Lindsay *et al.*, 1988).

During the Ice Age (2.4 million years ago), Scotland has witnessed several cold, 'glacial' periods followed by much shorter, warmer 'interglacial' periods, every 100,000 years or so; the last major glaciation peak in Scotland occurred about 22,000 years ago (Auton *et al.*, 2011). During deglaciation, smooth and gently undulating sheets of 'till' were deposited on the lower grounds. Around 11,500 years ago, as the Ice Age ended, thin stony soils developed on the sediments laid down by the glaciers, which are colonised by herbaceous plants and shrubs, and eventually much of the moorland became wooded (Auton *et al.*, 2011). In the Flow Country, clearance of forests by Mesolithic man coupled with a cooler and wetter climate led to the widespread development of the peat mosses, about 6,000 years ago (Belyea and Baird, 2006; Auton *et al.*, 2011).

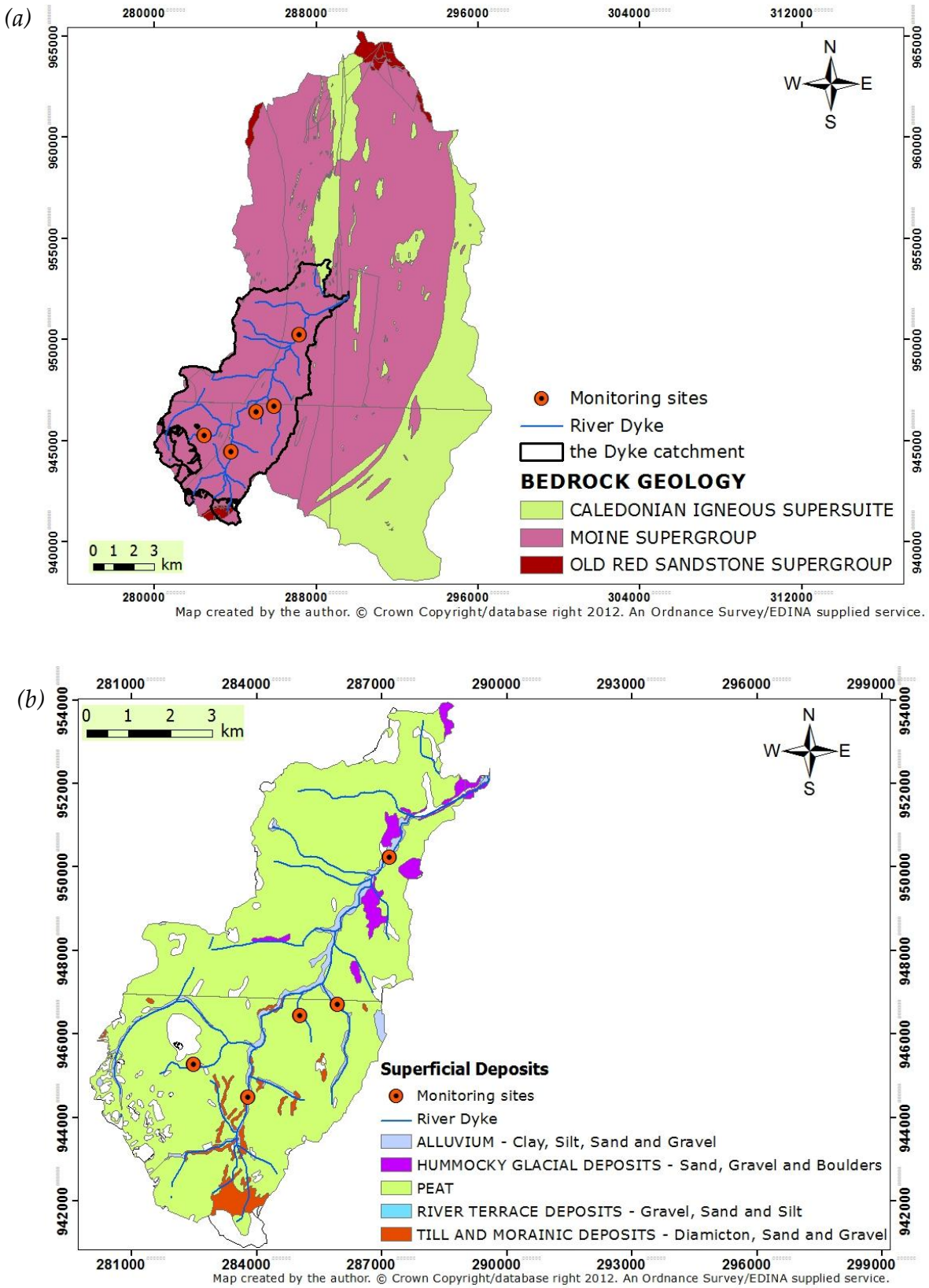


Figure 3.4: Maps showing (a) geology of the Halladale catchment, and (b) distribution of superficial deposits in the Dyke catchment.

Bedrock geology of the River Dyke catchment is overlain by glacial till and alluvium *(Figure 3.4b)*. The hills on the Sutherland-Caithness border (roughly along the River Halladale, see *Figure 3.1*) once supported an ice dome with a radial flow pattern, and Quaternary-aged till and glacio-fluvial deposits record the interactions between advancing and retreating ice sheets and topography (Gordon, 1993; Thomas *et al.*, 2004; McMillan, 2005; Auton *et al.*, 2011). The mixed type of superficial geology, which varies from stiff clay to loose sands and gravels, coupled with cool, humid climate, gentle topography and acidic substrates favoured the development of ombrotrophic peat bog (Lindsay *et al.*, 1988; Holden, 2005; Evans and Warburton, 2007).

Movement of retreating glaciers over the catchments scoured away loose and weathered rocks and over-deepened, widened and straightened pre-existing valleys (Lindsay *et al.*, 1988; Auton *et al.*, 2011). The upper River Dyke sections are deeply incised into alternating peat and glacial till layers *(Figure 3.13b)*. The channel width in this section range from one to 2.5 metres and the slope widely vary between 10 and 48 degrees. Slope decreases towards the centre and lower reaches of the river, ranging from 10 to 0 degrees. The channel width in the middle and lower sections of the River Dyke vary between 2.5 and 11 metres (at River Dyke Bridge site). The bed material vary widely as the clay, silt, sand and relatively angular pebbles dominate the upper sections, and relatively rounded pebble and cobble sized material predominantly occurring at the lower reaches. Tight meander train and bank erosion is common in the middle stretch of the River Dyke. In general, the River Dyke exhibits meandering with a cobble-bed channel and is entrenched towards the north with well-developed floodplain and pool-rifle sequences (Roberts, 2008) typical of glaciated valleys (Rosgen, 1996). As the River Dyke approaches the confluence with the Halladale River *(Figure 3.1)*, there is a well-developed

knickpoint and incised stretch of the river where the sudden increase in slope *(Figure 3.2)* results in a straight channel. The four major environmental controls, which may have determined the modern river Dyke morphology could be climate, geology, glaciation and time, as defined for the major Scottish rivers (Werritty and McEwen, 1997; Werritty, 2002).

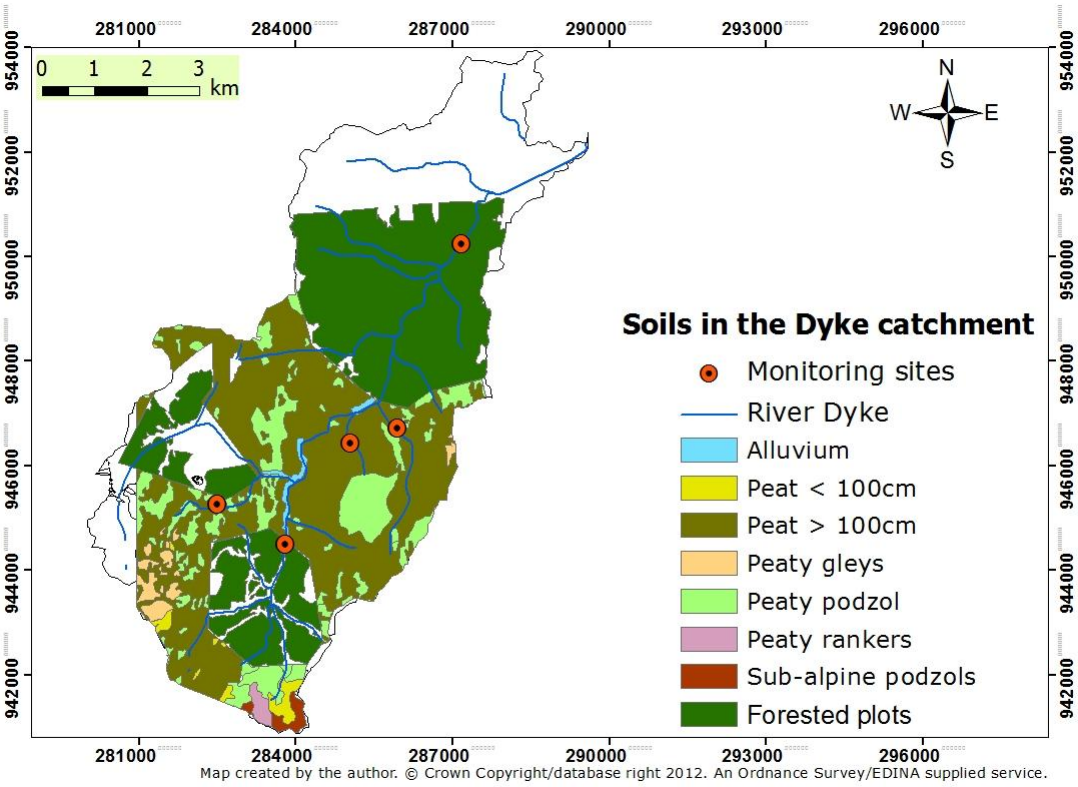


Figure 3.5: Map showing distribution of soils in the Dyke catchment; (soil data obtained from the RSPB).

The soils are typical of upland peat catchments and main soil types include thick (>100 cm) and thinned (<100 cm) peats, peaty podzols, peaty rankers, peaty gleys, and sub-alpine podzols (Boorman *et al.*, 1995; MLURI, 2010; Dobbie *et al.*, 2011). Their distribution across the River Dyke catchment is shown in *Figure 3.5;* however, data is unavailable for the top most part of the

catchment. Thick organic peat soils (>100cm) dominate about 80% of the River Dyke catchment with peaty podozols being the second largest soil type in the catchment. In the catchment, B-horizon is generally characterized by loamy sand that is underlain by glacial till (Gilbert, 2007; Roberts, 2008; RSPB, 2009).

Peat development on the valley floors is limited by inundation and erosion of the flood plains, and soils in these areas are relatively thin and well-structured podzols with a sandy loam texture (Lindsay *et al.*, 1988; Charman, 2002; Holden, 2005; Roberts, 2008). Peatland vegetation is dominated by mosses (*e.g., Sphagnum, Racomitrium lanuginosum*), sedges and small shrubs (Lindsay *et al.*, 1988). Hence, pH in the catchment is controlled by the release of organic acids and cation exchange by *sphagnum* moss (Wetzel, 2001) and acidic values of pH 4 are typical during high flows (Roberts, 2008). Although, biological processes in peat systems primarily control the production of DOC and hydrological processes control its export (McDowell and Likens, 1988), the solubility of DOC mainly depends on pH and ionic strength (Clark *et al.*, 2005).

Table 3.1: Summary of catchment characteristics for the sites.

Catchment characteristic	***Intact site***	***Forested site***	***Felled site***
Catchment area	0.7 km^2	9.0 km^2	3.2 km^2 & 0.95 km^2
Geology	Migmatitic psammite with migmatitic semipelite.	Migmatitic pelite and migmatitic semipelite.	Migmatitic pelite and migmatitic semipelite.
Soils	Peat and peaty podzols.	Peat, peaty podzol, peaty rankers & sub-alpine podzols.	Peat and peaty podzols.
Elevation	200 - 250 m	160 - 400 m	150 - 200 m
Slope	0 - 10^0	0 - 42^0	0 - 7^0

3.4. Monitoring Sites and Landuse

The Flow Country of Caithness and Sutherland is the UK's largest (400,000 ha) blanket bog, of which about 150,000 ha are 'severely affected' by landscape-scale drainage of the bog and non-native conifer planting. Therefore, major initiatives to restore these degraded areas are in place (LIFE Peatlands Project, 2005). As a part of LIFE Peatlands Project, the Royal Society for the Protection of Birds (RSPB) acquired Forsinard Estate (in the heart of the Flow country) in 1995, and have been carrying out extensive restoration through tree felling and drain-blocking. So far, 2,200 ha of forestry have been felled and drains have been blocked across 16,500 ha of bog in Forsinard Flows (RSPB, 2011). Currently under the UK Biodiversity Action Plan, the Blanket Bog Habitat Action Plan aims to restore 75% of degraded blanket bog by 2015 (LIFE Peatlands Project, 2005).

The Dyke catchment mainly comprises of areas of thick (>100cm) and thin (<100cm) peats, afforested plots, deforested plots (felled-to-waste, as a part of restoration) and various natural pools in the southwestern section of the catchment *(Figure 3.6a)*. Most of the catchment area (> 60%) is covered by open peatland *(Figure 3.6a)*, where the vegetation is dominated by mosses such as *Sphagnum*, *Racomitrium lanuginosum*, sedges and small shrubs. Therefore, a monitoring site (the intact site - NC 82495 45270) to represent near-pristine peatland was chosen in the southwestern part of the catchment where disturbance is minimal *(Figure 3.6)*. There are three drains running from a forested area to the Garbh Allt stream, however, care has been taken to avoid the influence of the drains on the streamwater by choosing the sampling site well upstream to any man-made structures. This monitoring point drains an upstream area of about 0.7 km^2 of intact peat *(Figure 3.6b)*.

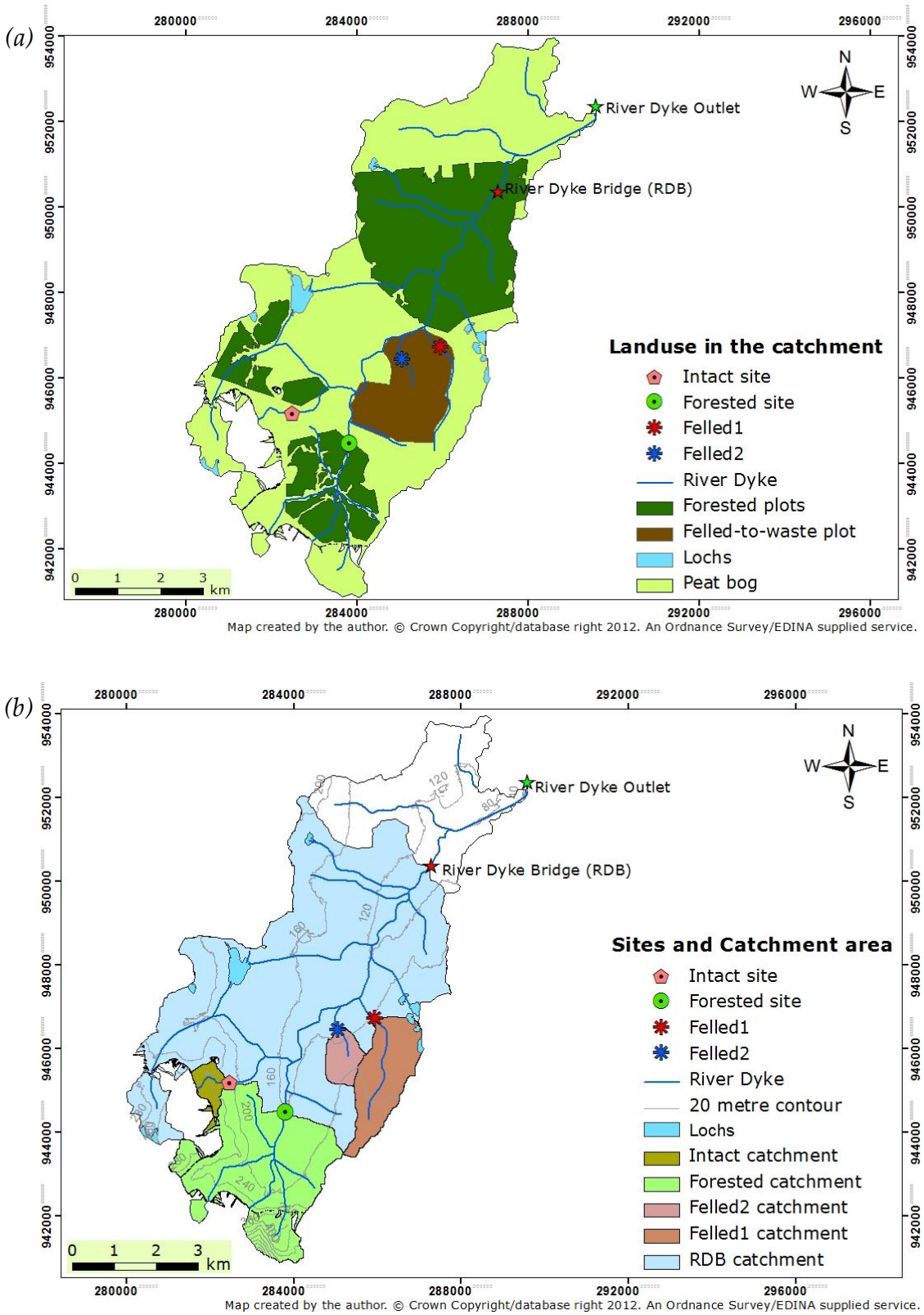


Figure 3.6: Maps showing monitoring sites and (a) Landuse, and (b) Upstream catchment area for sites.

The peatlands of Caithness and Sutherland have been tree-less for the majority of the last 8000 years (Gilbert, 2007). However, plantation of non-native conifers in the 1920's and forestry expansion in 1960's involved draining of peat bogs to lower the water table causing degradation in the natural bog system; afforestation in the Halladale catchment was initiated in the late 1970's (Marsh and Hannaford, 2008). In the Dyke catchment, plantation was planted between 1982 and 1990 and accounts for about 32% (~17.5 km^2) of the total catchment area *(Figure 3.6a)*, with a mixture of lodgepole pine (*Pinus contorta*) and sitka spruce (*Picea sitchensis*). A monitoring site (NC 83797 44493) in a forested plot, situated to the far south of the catchment, was chosen to represent drained and afforested peatland, and the area upstream of the point is about 9.0 km^2 *(Figure 3.6b)*.

Restoration procedures attempt to remove plantation trees (by clear felling or felling to waste) and/or to raise water levels by blocking rains, in order to allow the bog vegetation to thrive and return to the pre-disturbance state. The restoration and conservation of afforested plots in the catchment were initiated by the RSPB in 2004 by felling of forestry to waste *(Figure 3.10)* and drain blocking, during the second phase (2001 - 2006) of the LIFE Peatlands Project. Of the total forested area (19 km^2) in the catchment, about 4.6 km^2 has undergone tree felling *(Figure 3.6a),* and the drainage ditches in these plots have been blocked using a combination of peat dams and plastic inter-locking sheets *(Figure 3.11)*. In order to minimize the soil and sediment disturbance due to felling, heavy tree-felling machinery was replaced by three main felling techniques - i) motor manual felling using chainsaws, ii) hydraulic tree shear on a low ground pressure digger base, and iii) whole tree mulcher (RSPB, 2009). Two monitoring sites (NC 85941 46724 & NC 85045 46442) draining an

upstream area of 3.2 km² and 0.95 km² *(Figure 3.6b)* were chosen to study the effects of restoration on the aquatic export of carbon and stream water quality.

Other activities that may influence surface water quality in the catchment include small-scale cattle grazing, deer stalking, private fishing, bird watching and nature conservation (Wilkie, 2004).

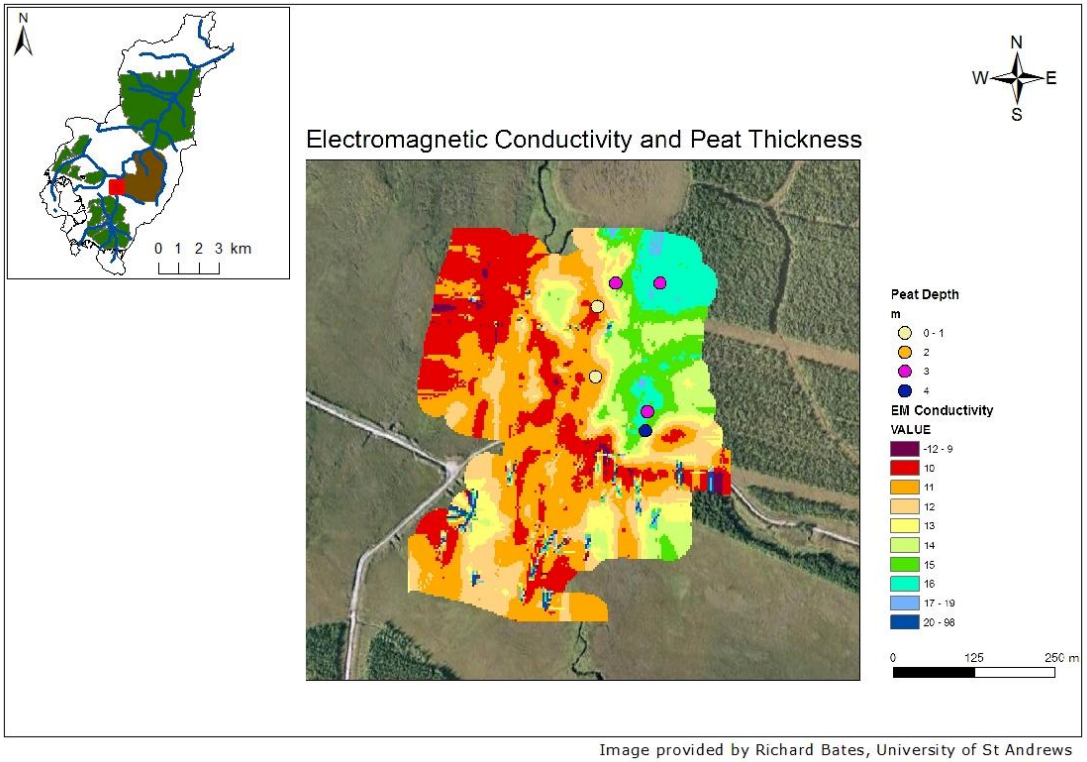


Figure 3.7: Image showing peat thickness a plot close to the monitoring sites. Site location in the catchment is shown in the inset.

Although there is only limited information available (only up to 100 cm depth) on the thickness peat in the Dyke catchment (see *Figure 3.5*). The recent geophysical investigations and peat core sampling carried out in the Dyke catchment, as a part of undergraduate field training, revealed that peat thickness in the catchment vary between 0 and 4 metres *(Figure 3.7)*.

(a)

(b)

Figure 3.8: (a) The intact catchment and (b) sampling site during a storm event, looking downstream. Location of the site shown in the inset.

(a)

(b)

Figure 3.9: (a) The forested catchment (b) and sampling site looking upstream. Location of the site shown in the inset.

(a)

(b)

Figure 3.10: (a) and (b) Overview of elled-to-waste plots in the Dyke catchment (view to the south). Location of the site shown in the inset.

(a)

(b)

Figure 3.11: Blocked drain in a felled-to-waste plot s using PVC sheets (installed by RSPB) during (a) low flow and (b) after a storm event.

(a)

(b)

Figure 3.12: (a) the River Dyke Bridge (NC 87178 50254) downstream sampling site just upstream of the confluence (looking downstream, and (b) the confluence (NC 89576 52370) of the River Dyke with the River Halladale (looking upstream on the Halladale). Location of sites shown in the insets.

(a)

(b)

Figure 3.13: Exposed peat horizons showing (a) thick (>100cm) upper layers of peat in an intact bog, and (b) bank erosion at a downstream site inf the forested sub-catchment.

(a)

(b)

Figure 3.14: (a) The River Dyke bridge site at low flow, and (b) the main stem of the River Halladale at Forsil (both looking upstream)

Chapter 4
MATERIALS AND METHODS

This chapter describes the analytical methods adopted in this research project, including the strategies and methodologies of sample collection, and laboratory techniques used. It also explains why these methodologies were selected, and the rationale for the procedures adopted.

4.1. Sampling design:

A reconnaissance survey in the River Dyke catchment was carried out on 06 Mar 2009 and 07 Mar 2009, prior to designing a sampling programme. This survey comprised of: i) identifying appropriate sampling sites in the intact peatland, drained and forested peatland, and felled-to-waste plots in the catchment, ii) finding suitable sites for the installation of data loggers, stage boards and automatic water samplers, iii) initial water sample collection at four locations on the River Dyke and one location on the River Halladale, and iv) undertaking pH, conductivity and dissolved oxygen measurements at all sites over two days. Based on the initial findings, three appropriate sampling sites were chosen which represent different land-use areas of peatland in the central region of the Dyke catchment, and a forth site further downstream on the River Dyke was chosen to monitor the catchment-integrated concentrations of DOC as a function of catchment size *(Figure 4.1)*. To monitor downstream impacts of the River Dyke on the Halladale River, an additional four sites were chosen on the main stem *(*see *Figure 4.1)* which were sampled occasionally. Permission to conduct the project was granted by the RSPB (Forsinard), and they guided site selection and allowed access to the sites. The Strath Halladale Partnership allowed unlimited access to the salmon beats on the Halladale and assisted with equipment installation and sampling.

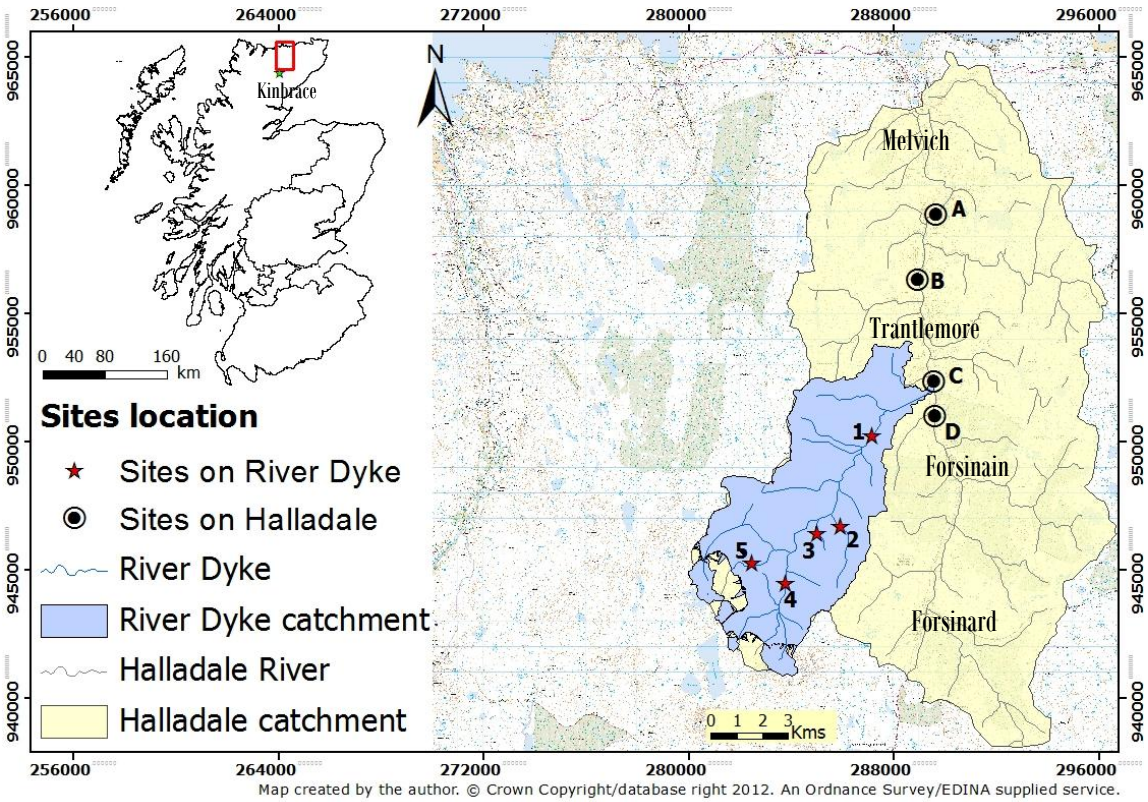


Figure 4.1: Map showing location of sites on the River Halladale (A - NC 89658 58878, B - NC 88940 56327, C - NC 89576 52370 & D - NC 89597 51015), and on the River Dyke (1 - NC 87178 50254, 2 - NC 85941 46724, 3 - NC 85045 46442, 4 - NC 83797 44493 & 5 - NC 82495 45270).

4.2. Sampling strategy

Sites and their locations in the catchment are shown in *Figure 4.1*, and listed in *Table 4.1*. Sites 2, 3, 4 and 5 are the main monitoring sites that represent different landuse areas, and are sampled intensively during storm events; sites A, B, C and D are located on the Halladale River *(Figure 4.1)*.

Blanket bog streams typically have a very flashy and responsive hydrograph (Evans *et al.*, 1999; Holden and Burt, 2003), and most of the chemical changes in the water occur during storm events that may not be captured by weekly or fortnightly sampling intervals. Approximately 50% of the total DOC export occurs during the upper 10% of the flow values and many sampling programmes thus underestimate the total DOC export as they miss at

least some of the high flow events (Schiff *et al.*, 1998). It was therefore deemed necessary to carry out more intensive event sampling campaigns in order to include as many peak discharge periods as possible. , A sampling strategy was developed to monitor the changes in stream water chemistry related to changes in flow paths and runoff, with higher frequency sampling of high discharge events, and less frequent sampling of low flow events to allow the base flow chemistry to be measured.

Fieldwork was carefully planned in May 2009 well in advance of the commencement of monitoring period 1 (August 2009). On analysing the SEPA 10-year discharge record (1998-2008) for the Halladale River (SEPA-North, 2008), storm events last for a minimum of 24 hours and a maximum of 4 days. At each of the main monitoring sites, intensive sampling comprised two-hourly intervals during high discharge events *(*Table 4.2*)*, in order to capture changes in water chemistry as the event progressed and to investigate flow-related variations in the stream water chemistry during individual storm events. During base flow conditions, twelve-hour sampling intervals were initially chosen, but this was later reduced to six-hour intervals to ensure a better coverage of temporal variability in streamwater chemistry, and to avoid any data gaps. Precipitation data for the same period as discharge suggests a lag of 8 - 24 hours between the onset of rainfall and an event response on the hydrograph depending on the antecedent moisture conditions. Therefore, storm event sampling (2-hourly) was generally set to begin several hours prior to the anticipated rainfall whenever possible. However, given the rapid response of the sites to storm events, and because of access problems due to the distance to, and between, sites, it was often found difficult to sample the earlier stages of an event.

Table 4.1: Monitoring sites, landuse and location on the River Dyke and on the main stem (Halladale River)

Site	Landuse	Location
1	Mixed (bog and forestry)	River Dyke bridge - a downstream site (drains 44.4 km^2) close to the outlet of the River Dyke (NC 87178 50254)
2 & 3	Forestry felled to waste (2004 - 2006) and drains blocked	Drains (0.95 km^2) felled forestry. Site 2 - (NC 85941 46724) 3.8 km^2 and site 3 - (NC 85045 46442)
4	Afforested peat	Drains (9 km^2) Upper River Dyke forest (NC 83797 44493)
5	Intact peat bog	Drains (0.69 km^2) near-pristine peatland (NC 82495 45270)
D	Mixed - River Halladale	Before River Dyke's confluence with the main stem (NC 89597 51015)
C	Mixed - River Halladale	Just after the confluence with the main stem, at the Cemetery (NC 89576 52370)
B	Mixed - River Halladale	A downstream site near the Bighouse (NC 88940 56327)
A	Mixed - River Halladale	A further downstream site near Forsil (NC 89658 58878)

4.3. Streamwater Sampling

Storm event and low flow sampling was undertaken at different seasons between August 2009 and April 2011. Additional spot samples were collected from the three main sites in between the intensive monitoring periods whenever possible during July - November 2010 and January - March 2011, as listed in *Table 4.2*.

Main sites were gauged (see *section 4.1*) and water samples were collected close to the gauging stations, except for the forested site where the stage logger is ~200m downstream from the water sampling site. Bühler 1000 automatic samplers with 24 one-litre containers *(Figure 4.2)* were deployed at each site. Containers were cleaned thoroughly by rinsing with dilute reagent grade (0.01M) nitric acid (HNO_3) followed by rinsing twice with stream water, after each sampling cycle. The sampling hose was anchored against the stage board pole or a solid rock nearby to ensure i) the end of the hose was not touching any bed sediment, ii) that the sampling was always done in a fully mixed part of the flow, and iii) sample collection was conducted from the same point each time. Water samples were collected (or transferred from the sampler container) in 250 ml polyethylene bottles that were pre-rinsed with dilute acid (0.01M HNO_3). All bottles were labelled by a site - identifier, date and time of sample collection.

At each sampling site, *in situ* readings of pH, conductivity, dissolved oxygen and water temperature were taken using Hach Lange Intellical HQ30d probes (see *Appendix I* for detection limits and accuracy). These readings are automatically corrected to room temperature (25^0 C). GPS co-ordinates, time of sampling, stage level from the stage board at each site, and other relevant information were recorded in a field notebook, including a brief summary about the weather conditions in the catchment on the sampling day.

Table 4.2: Streamwater sampling frequency, monitoring periods and number of samples collected from sites

Monitoring Period	Sampling Period	Sampling Interval	Sampling Sites	Total no. of samples
1	01 Aug 09 – 28 Aug 09	2-hourly, 12-hourly	Sites 1, 2, 4, 5, A, B, C, D	331
2	24 Apr 10 – 28 Apr 10	2-hourly	Sites 1, 2, 3, 4, 5, A, B, C, D	76
3	07 Jul 10 – 10 Jul 10	2-hourly	Sites 1, 2, 3, 4, 5, A, B, C, D	52
4	26 Jul 10 – 31 Jul 10	2-hourly, 6-hourly	Sites 1, 2, 3, 4, 5, A, B, C, D	97
5	23 Aug 10 – 30 Aug 10	2-hourly, 6-hourly	Sites 1, 2, 3, 4, 5, A, B, C, D	132
6	03 Apr 11 – 08 Apr 11	2-hourly, 6-hourly	Sites 1, 3, 4, 5, A, B, C, D	104
N/A	June, July, Aug, Sep, Nov 2010; Jan, Feb and March 2011	Grab samples – once in a given day	Sites 1, 3, 4, 5	114
			TOTAL	906

Sampling intervals were almost the same for the three main sites (2 - 5), but differ for the other sites (1, A-D) which limits the comparison of the main sites with those downstream, , but can still allow the spatial variability in stream water chemistry to be investigated. A long, continuous sampling period in August 2009 provided a wider range of flows, including two significant storm events of intermediate intensity. Low flow conditions were sampled during 26 – 30 July 2010 following a dry summer period; highest flows were sampled during September 2010 (spot sampling). Most of the samples were collected during small to intermediate (0.8 to 9 mm) rainfall events or in

between rainfall events *(Figure 4.3)*. Sampling covered a wide range of discharges, however sometimes significant changes in stream chemistry were noted when stream discharge did not vary significantly. On some occasions, stream chemistry varied widely for similar amount of discharges, due to seasonal variations. Thus, sampling has also captured different seasons or times of the year *(Table 4.2 and Figure 4.3)*.

(a)

(b)

Figure 4.2: Bühler 1000 automatic water sampler (a) outside view, and (b) inside view

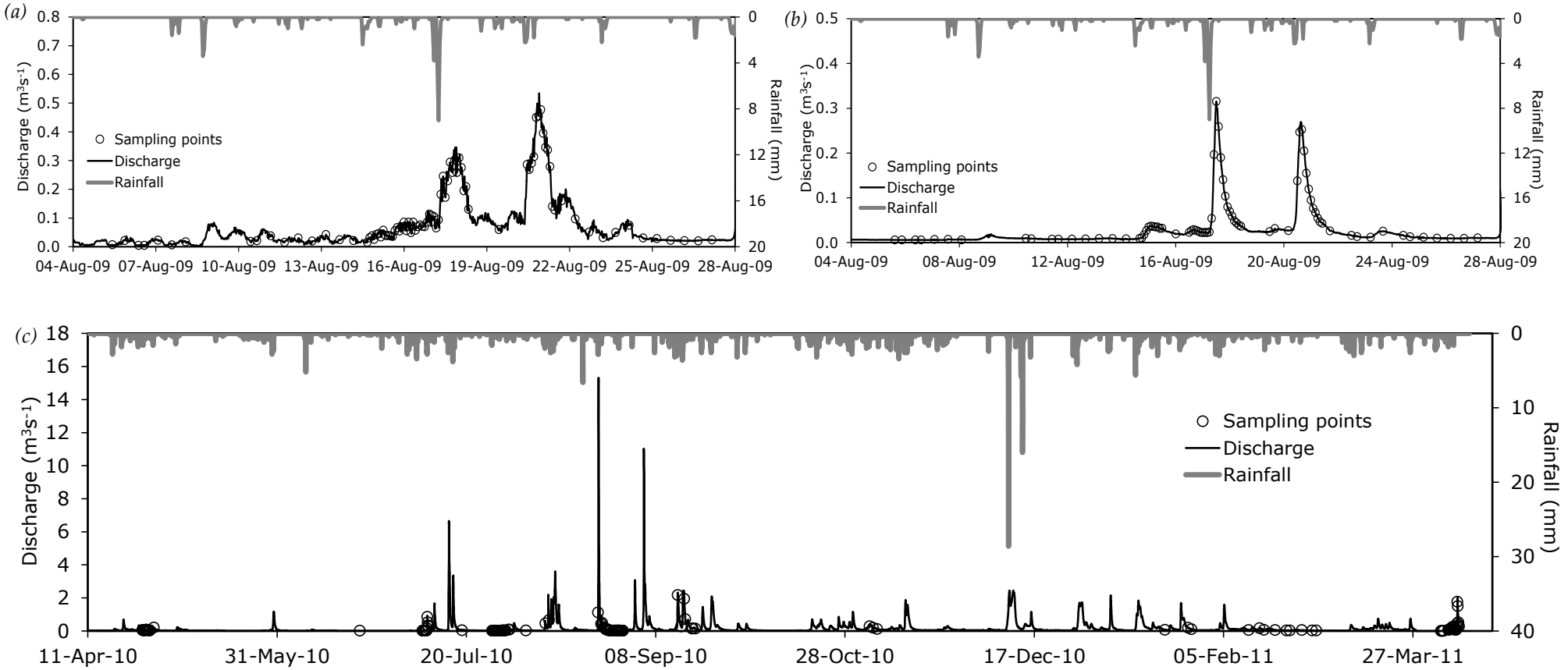
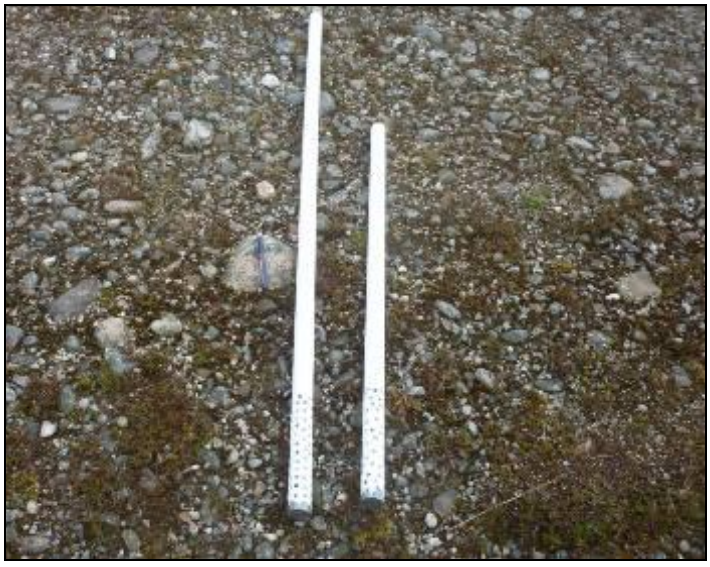


Figure 4.3: Sampling times with stream discharge and rainfall at all main monitoring sites: a) Intact site (2009), b) Forested & Felled sites (2009), and c) All sites (2010 & 2011).

Problems encountered during the sampling periods were mainly related to weather conditions (deep snow) and deer counting seasons, which impeded access to the sites. Sampling was sometimes disrupted due to the malfunction of the auto-samplers during continuous monitoring periods. It was sometimes difficult to anticipate and plan the field trips to coincide with the storm events, however, at such times spot samples were collected during high discharges by the Strath Halladale Partnership river manager (Mr Willie Grant).

(a)



(b)

Figure 4.4: (a) PVC tubes (with sealed lower ends) used as tube wells for soilwater sampling, and (b) perforations made at the lower 20cm of each tube.

4.4. Soilwater sampling

In order to monitor soil water chemistry, tube ("piezometric") wells were made using PVC tubes (13 mm diameter) of different lengths (55cm, 105cm and 155cm) with perforations drilled in the lower 20cm of each tube. These tube wells were nested in two sets at each site to collect soil water samples from 30-50cm, 80-100cm and 130-150cm depths within the soil profile. Approximately 5 cm of each tube was always above the ground surface. These piezometric well sites are located close (5 – 10 meters) to the streamwater sampling sites (see *Figure 4.1*). Soil water samples from the tube wells were collected occasionally, in clean acid-rinsed and labelled 125ml Nalgene bottles using rubber tubing and a 50ml syringe to extract the soil water. To ensure sampling of fresh soilwater, water in the wells was completely emptied a day prior to sampling. During the study period, 45 soilwater samples were collected from all the sites together as shown in *Table 4.3*.

Table 4.3: Soilwater sampling frequency, and number of samples collected from sites

Site	Date of sampling	Total no. of samples
Intact	25 Aug 2010	6
	29 Aug 2010	4
	04 Apr 2011	6
Forested	25 Aug 2010	6
	29 Aug 2010	5
	04 Apr 2011	5
Felled	25 Aug 2010	4
	29 Aug 2010	5
	04 Apr 2011	4
	TOTAL	*45*

4.5. Sample treatment and analysis

Samples were taken immediately after collection to a field laboratory, constructed in the garage of the Estate Office of the Strath Halladale Partnership at Forsinard, for filtration, absorbance analysis and treatment. All samples were filtered using vacuum pumps *(see Figure 4.5a)* through pre-combusted Whatman GF/F grade 0.7 micron filters. Filtration was done within 24 hours of collection, except for the spot samples collected in between the intensive monitoring periods which were filtered within 48 - 72 hours (depending on shipping time). These samples were acidified prior to shipping to minimize any sample deterioration. Filter papers trapping sediment (greater than 0.7microns) were stored in plastic petridishes and kept in a deep-freezer at St Andrews until they were analysed for particulate organic carbon (POC).

Multi-wavelength absorbance measurements were made for each filtered sample using a portable Hach Lange DR 2800 spectrophotometer *(Figure 4.5b)* in order to use absorbance as a proxy for DOC estimation. After the absorbance measurements, each sample was homogenized by thorough shaking before splitting it into two aliquots. Aliquots for dissolved organic carbon analysis (DOC) were acidified with concentrated (98% grade) sulphuric acid (H_2SO_4) to pH 2-3, to minimize sample deterioration until further analysis (Kaplan, 1994), and samples were exposed to fresh air to purge out any inorganic carbon. Samples for major, minor and trace element analysis were acidified to pH ≤ 2 with concentrated reagent (70%) grade nitric acid (HNO_3) to supress metal precipitation and sorption processes until analysis. All samples were then kept refrigerated below 4^0C until further analysis.

(a)

(b)

Figure 4.5: (a) Water sample filtration using vacuum pumps, and (b) Hach Lange DR2800 portable spectrophotometer used to measure absorbance of water samples.

4.5.1. Dissolved organic carbon (DOC) analysis

4.5.1.a. DOC analysis of water samples

Dissolved organic carbon (DOC) was measured using a Thermalox® Total organic carbon (TOC) analyser at University of Glasgow, which has a precision of ± 0.1 mgC L^{-1}, a minimum detection limit of 1.0 mgC L^{-1} and a maximum limit of 100 mgC L^{-1}. About 4ml of each acidified water sample *(see Section 4.5)* is

taken in a clean 4 ml glass vial and injected over a platinum-coated, mesh catalyst. Three replicate injections (up to 100µL each) were performed for each sample. Thermal catalytic oxidation at 680^0C with oxygen carrier gas was used to oxidise carbon compounds to CO_2, which is then detected and measured using a non-dispersive infrared detector. Standards made of a potassium-hydrogen-phthalate solution ($C_8H_5KO_4$) and known concentrations of 10 to 40 mgC L^{-1} were used for calibration and for quality control standards. Calibration curves between absorbance and measured DOC_m concentration were developed to estimate DOC_e concentrations using absorbance.

4.5.1.b. Dissolved organic carbon - Absorbance Analysis

Generally, it is widely recognised that dissolved organic carbon is a vital component of water systems and much of the colour in water is due to the presence of humic acids leached from plant and soil organic matter (Thurman, 1985). While absolute DOC concentrations can be measured directly on various TOC analysers, the high-resolution monitoring of DOC conducted in this project means that a less time consuming and inexpensive method is preferable. Aquatic DOC is mainly comprised of humic and fulvic acids, which make the largest contribution (75-80%) to DOC in stream waters (Thurman, 1985); these components of DOC strongly absorb light which allow estimation of DOC concentrations from absorbance measurements. Several studies have used absorbance as a proxy to estimate DOC in streamwater samples (Grieve, 1985; Collier, 1987; Moore, 1987; Worrall *et al.*, 2002; Spencer *et al.*, 2007b; Wallage and Holden, 2010; Grayson and Holden, 2011). Most of these studies involve absolute measurements of DOC, using TOC analysers, to establish a relationship between absorbance and DOC. For example, Worrall *et al.* (2002) have observed a strong linear relationship between DOC and absorbance at both 400 and 436 nm wavelengths. Many other studies have found a similar relationship using 340, 360, 365, 410, 465 and 470 nm (Tipping *et al.*, 1999;

Kalbitz *et al.*, 2000; Wallage *et al.*, 2006; Spencer *et al.*, 2007a; Baker *et al.*, 2008). However, Wallage and Holden (2010) doubt the use of absorbance at a single wavelength as a proxy for DOC and suggest that the DOC thus estimated is dependent on the calibration used. Moreover, humic and fulvic acids absorb different amounts of light at different wavelengths which indicates the maturity of DOC as humic acids are more mature or relatively older than fulvic acids.

In this study the absorbance of (stream and soil) water samples was measured at 360, 400, 465, and 665 nm wavelengths immediately following the filtration, using a Hach DR2800 portable spectrophotometer *(Figure 4.5b),* which has a precision of ± 0.002 absorbance units. Refrigerated samples were left to equilibrate to room temperature before analysis (wherever applicable). A clean quartz cell with a 1-inch path length was used for each sample and de-ionised water was used as a blank. After each absorbance measurement, a blank was used to zero the reading to ensure minimal drift, and duplicate analyses were performed for every 15-20 samples to ensure instrument stability. Limit of detection and uncertainties are provided in *Appendix I***.**

Table 4.4: DOC and absorbance relationships at 400 nm wavelength

Site	Min Res[a]	Max Res[a]	N	R^2	Relationship	SE
Pooled	-15.0	12.8	185	0.91	DOC = 65.1 A_{400} + 3.2	4.7
Intact	-8.4	9.5	65	0.82	DOC = 78.6 A_{400} + 0.8	3.7
Forested	-4.2	11.0	52	0.88	DOC = 88.5 A_{400} - 5.7	3.2
Felled	-14.6	8.6	68	0.86	DOC = 68.7 A_{400} - 0.4	5.4

[a] The minimum and maximum differences (residuals) between predicted and actual DOC;
SE - standard error of the residual

While 360 and 400 nm wavelengths were used to establish a relationship between absorbance and DOC_m (measured), absorbance values at 465 and 665 nm are used to estimate E4/E6 ratio. This ratio is 2-5 for more mature humic acids and is 8-10 in relatively less mature fulvic acids (Thurman, 1985; Wallage *et al.*, 2006). Absolute DOC_m concentrations of samples, measured using the TOC analyser, are compared against the absorbance values as shown in *Table 4.4, Table 4.5 & Figure 4.6*.

Spearman's Rank correlations between DOC and absorbance at 360nm (A_{360}) and 460nm (A_{400}) were performed which yielded similar results for both the wavelengths used *(Table 4.4 & Table 4.5*). The slopes of the regressions for each wavelength show similar rankings, with felled, intact, and forested sites having lowest, intermediate and highest slopes, respectively.

Table 4.5: DOC and absorbance relationship at 360 nm wavelength

Site	Min Res[a]	Max Res[a]	N	R^2	Relationship	SE
Pooled	-12.5	11.8	185	0.92	DOC = 34.1 A_{360} + 3.4	4.4
Intact	-7.8	7.5	65	0.84	DOC = 43.2 A_{360} + 0.02	3.5
Forested	-4.3	11.0	52	0.88	DOC = 47.3 A_{360} - 6.2	3.2
Felled	-12.0	7.2	68	0.90	DOC = 36.5 A_{360} - 1.1	4.5

[a] The minimum and maximum differences (residuals) between predicted and actual DOC;
SE - standard error of the residual

Table 4.4 & Table 4.5 show that there is a significant correlation ($p<0.001$ and r^2 = 0.91 and 0.92) between DOC and absorbance in the pooled dataset (n=185) taken from the three main sites. Although a strong positive relationship between DOC and absorbance is apparent from *Figure 4.6*, the graphs show that the DOC values that fall between 30 and 50 mg C L^{-1} slightly diverge from the regression line, which could be due to different sources of DOC for each site. For this reason, the data from each landuse site was analysed (*Figure 4.6 c & d).*

The pooled data trend is controlled by the felled site (highest DOC values) and the intact site values have less range, with a cluster around 30 mgC/L. The regression lines for the forested and intact sites are slightly offset, highlighting that the absorbance-DOC relationship does vary slightly between the different landuse types.

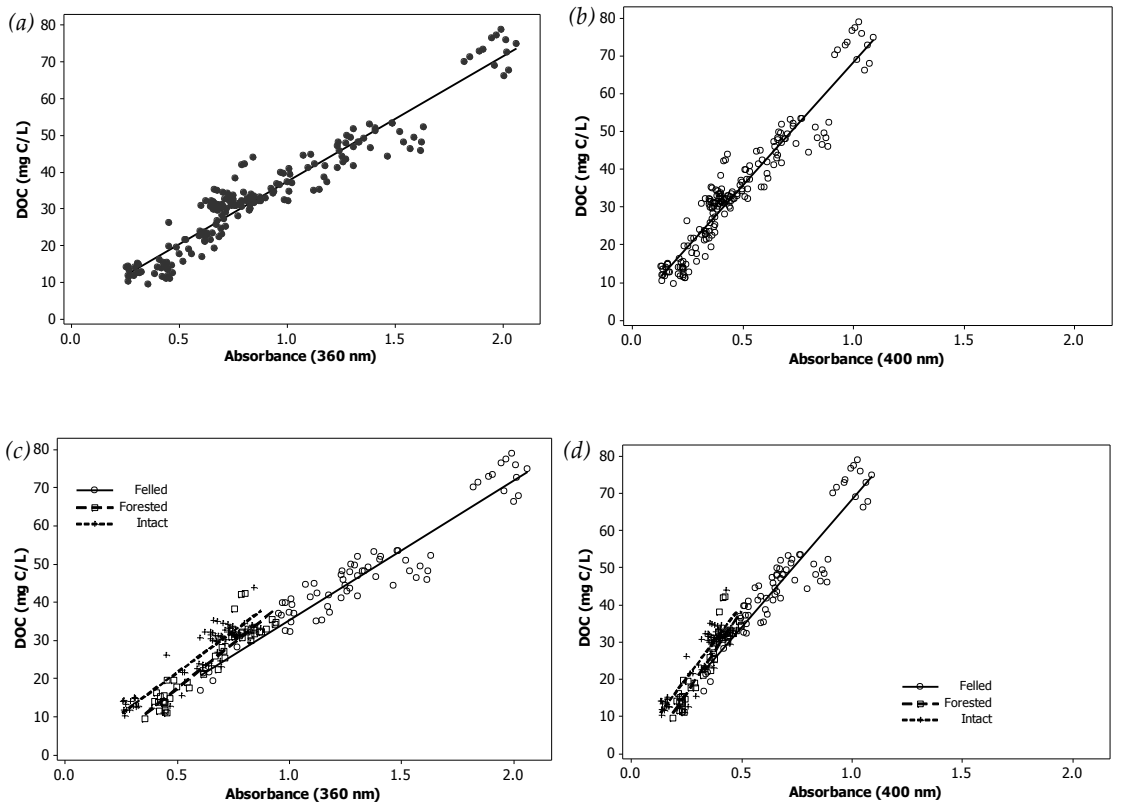


Figure 4.6: Plots showing the linear relationship between dissolved organic carbon (DOC), and absorbance at 360nm (left) and 400nm (right). (a) & (b) regression fit for pooled data (from all sites), and (c) & (d) site-specific regression relationship

In order to determine which absorbance wavelength best predicts DOC, the site-specific data and regressions for both absorbance wavelengths were compared (*Figure 4.7).* The level of absorbance decreases with increasing wavelength, such that absorbance at 360nm (A_{360}) may provide better precision for DOC than the 400nm estimator, even though A_{400} is more sensitive to DOC variation.

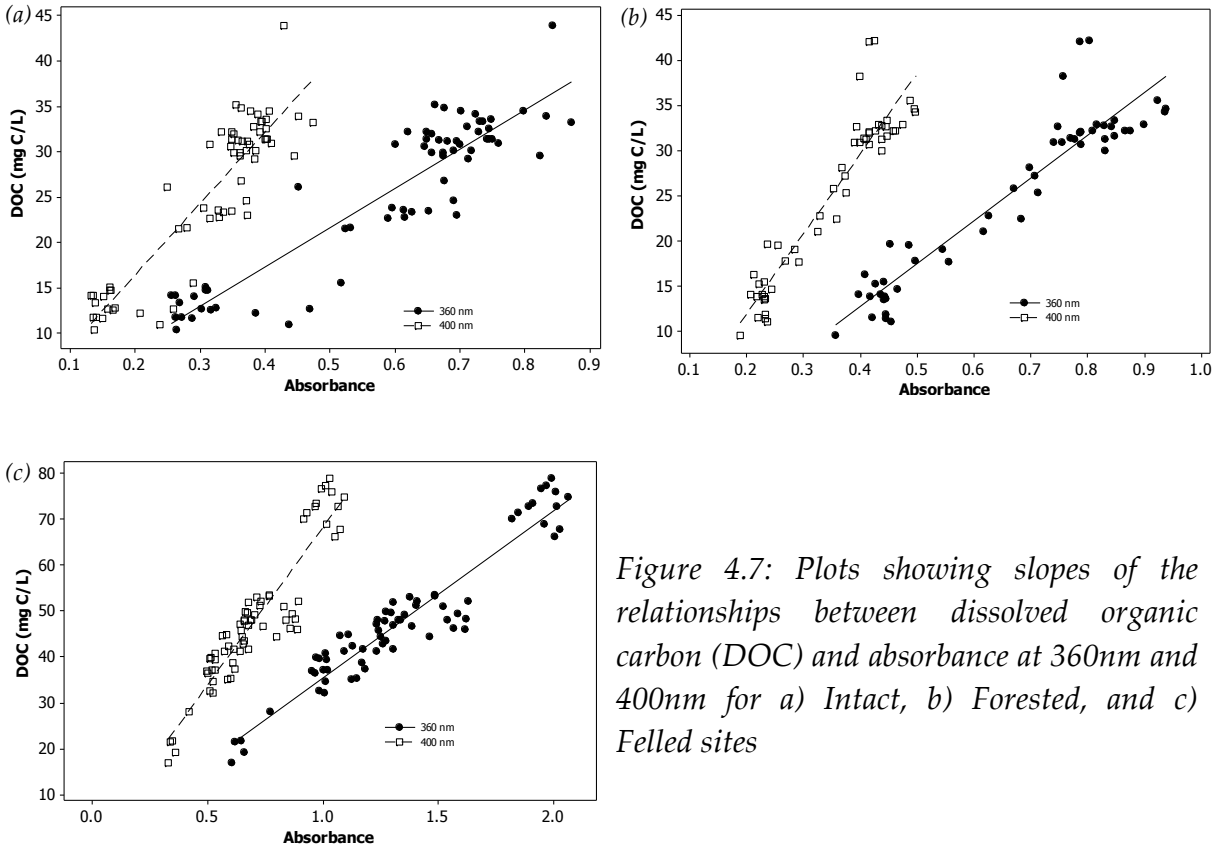


Figure 4.7: Plots showing slopes of the relationships between dissolved organic carbon (DOC) and absorbance at 360nm and 400nm for a) Intact, b) Forested, and c) Felled sites

Although a good correlation between streamwater colour (A_{360} and A_{400}) and DOC is evident at all sites, standard error, minimum and maximum residuals, and R^2 values are slightly better for A_{360} than for A_{400} (*Table 4.4 & Table 4.5*). In addition, the regression intercepts for A_{360} are lower than for A_{400} *(Table 4.4 & Table 4.5)*, indicating that most of the DOC is in a form that readily absorbs light at 360nm and is therefore coloured, while higher intercept values indicate that a portion of the DOC does not absorb light at 400nm and is un-coloured (Wallage and Holden, 2010). Therefore, the A_{400} regression may underestimate DOC concentration, and the A_{360} regression is used to estimate DOC concentration for any samples not analysed for TOC, and for calculating the total DOC budget from the hydrograph.

Many studies have demonstrated that although coloured humic substances make up the dominant fraction of DOC in water, their contribution

can vary between 30% and as much as 90%, with un-coloured non-humic compounds (e.g. amino-acids, proteins, and fats etc.) forming the rest of DOC (Thurman, 1985; Qualls and Richardson, 2003). Thus, estimating DOC concentrations from an absorbance - DOC relationship may result in significant underestimation (Wallage and Holden, 2010). In this study, absorbance has been calibrated with direct measurements of DOC made using a standard TOC analyser, and the resulting relationship therefore incorporates both humic and non-humic sources of DOC *(Figure 4.8)*. For example, when the intercept in A_{360} regression *(Table 4.5 & Figure 4.7a)* for the intact site (0.02 mg C L^{-1}) is taken as a proportion of the mean (measured) DOC concentration for this site (25.4 mg C L^{-1}), it suggests that A_{360} accounts for almost all the mean DOC with only 0.08% non-humic substances are left unaccounted for. Similarly, for felled and forested sites, negative values suggest that the water may be depleted of DOC when the absorbance or colour is zero, which implies that the DOC at these sites is made up of coloured humic substances alone and this is reflected in higher R^2 values *(Table 4.4 & Table 4.5)*. Hence, using absorbance as a proxy for true DOC determination is justified for this study.

4.5.2. Particulate organic carbon (POC) analysis

Direct determination of particulate organic carbon (POC) is not possible because of its complex chemistry and mixing with inorganic soil constituents, therefore indirect methods are generally used (Christensen and Per Åkesson Malmros, 1982; Heiri *et al.*, 2001). The loss-on-ignition (LOI) method involves combustion of sediment samples at high temperatures and measurement of weight loss after ignition and is a relatively inexpensive, quick, and precise way to predict POC (Lowther *et al.*, 1990; Konen *et al.*, 2002).

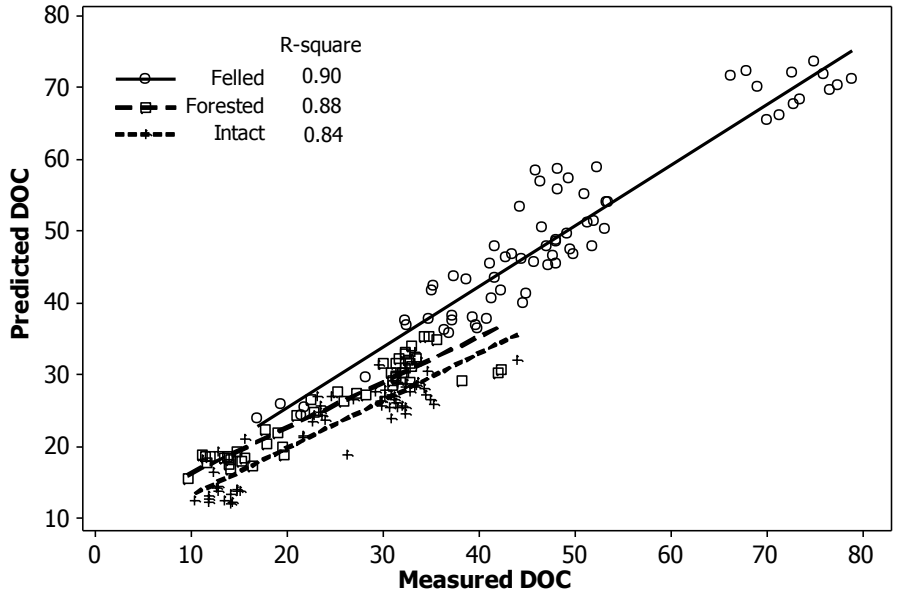


Figure 4.8: Predicted DOC (from absorbance at 360 nm) and measured DOC plot showing strong linear relationship and high R-squared values.

A few studies have questioned the use of the LOI method and two main sources of error that can occur during combustion have been identified: i) potential loss of CO_2 from inorganic matter in the sediment, and ii) loss of structural water from clay minerals (Ball, 1964; Dankers and Laane, 1983; Abella and Zimmer, 2007; Frangipane *et al.*, 2009). However, studies dealing with non-calcareous soils found that organic carbon concentrations determined by LOI were very close to that measured using a CHN (elemental) analyser (Ball, 1964; Howard and Howard, 1990; Craft *et al.*, 1991; Frangipane *et al.*, 2009).

In this study, filtered particulate matter was always less than 5mg, and given the number of samples (~900), the loss-on-ignition method was deemed appropriate to determine particulate organic concentrations. Filter papers and sediment were initially oven dried at 105^0C for 12 hours to eliminate hygroscopic water and ensure accurate sediment weight measurements (Eaton *et al.*, 2005). Samples were then combusted in a pre-heated muffle furnace at 550^0C for 4 hours (Christensen and Per Åkesson Malmros, 1982; Heiri *et al.*,

2001; Lyons *et al.*, 2002; Eaton *et al.*, 2005; Sarkhot *et al.*, 2007) and weight loss on ignition was determined on the combusted samples, assuming 58% of the weight lost is carbon (Broadbent, 1953; Ayub and Boyd, 1994; Nelson and Sommers, 1996; Sarkhot *et al.*, 2007). The equations used for POC estimation are provided in *Appendix I*.

4.5.3. Major, minor and trace element analysis

A full suite of major and minor ions, and trace metals analyses were performed on water samples using a Thermo X-series® Inductively Coupled Plasma Mass Spectrometer (ICP-MS), which is a part of CERSA(Centre for Earth Resources at St Andrews), with the assistance of senior technician Angus Calder. ICP-MS is a quick and highly sensitive multi-elemental analytic technique usually used for the quantification of total analyte concentrations (Jarvis *et al.*, 1992; SW-846 On-Line, 2007) and is well suited for samples that need low detection limits *(*see *Table 4.6).* Information regarding system specifications, functioning and operation of the instrument can be found on the Thermo Scientific website (http://www.thermoscientific.com). The following section provides an overview of the sample preparation and analysis procedure. The elements listed in *Table 4.6* were measured and the lower detection limits for the elements are shown in *Table 4.6*.

Sample Preparation

For ICP-MS analysis, samples should normally be filtered, free from sediment, and acidified to typically 2 % w/v HNO_3, in order to avoid blockage of the system and to optimize the performance of the instrument. In addition, the concentrations of the analysed elements in the samples had to be within the calibration range of the method in order to obtain reliable results (Jarvis *et al.*, 1992).

Table 4.6: Lower detection limits of some of the elements analysed by the Thermo X-series ICP-MS system.

Analyte	Detection limit (in ppb)
Aluminium (Al)	0.02
Antimony (Sb)	0.0006
Arsenic (As)	0.004
Barium (Ba)	0.004
Beryllium (Be)	0.002
Calcium (Ca)	0.6
Chromium (Cr)	0.005
Cobalt (Co)	0.0005
Copper (Cu)	0.002
Iron (Fe)	0.9
Lead (Pb)	0.0004
Magnesium (Mg)	0.02
Manganese (Mn)	0.008
Nickel (Ni)	0.003
Potassium (K)	2
Silicon (Si)	0.1
Sodium (Na)	0.2
Strontium (Sr)	0.0004
Titanium (Ti)	0.01
Vanadium (V)	0.003
Zinc (Zn)	0.02

Water samples for major, minor and trace element analysis were filtered and preserved with reagent grade concentrated HNO_3 *(see Section 4.5).* Since the major cation and metal concentrations in the samples were anticipated to be significantly higher than the calibration range of the method, dilution of the samples was necessary. Five ml of each sample is diluted with 5 ml of a

standard solution, containing 5% HNO_3 and 20 ppb of stock solution (Bi, Ho, In, Li, Rh, Sc, Tb, and Y), in a clean 15 ml analysis vial.

Sample Analysis

A full suite of analyses included major cations (Ca, Mg, N and K), dissolved metals (Al, Fe, Mn, Cu, Zn, Pb, Ni, Ti, Cr, and V), and SiO_2. A linear calibration method was adopted, which results in a calibration curve given by a linear combination of concentration (X) of the analyte and the intensity (Y) of the plasma. The details of calibration method, and range and precision of the elements analysed are provided in *Appendix I*.

4.6. Stage level monitoring and discharge measurements

4.6.1. Stage level data

During a reconnaissance survey in March 2009, the felled (site 2), forested and intact sites were chosen for continuous stream level monitoring. In June 2009, stage boards and Isodaq VF series data loggers (pressure transducers) were installed in still wells at each site *(Figure 4.9)*. Each logger is calibrated using the stage level read from the stage boards and set up to record stage level at 30-minute intervals. The logger installed at the forested site *(Figure 4.9b)* has a dual channel capability with a temperature sensor in addition to the pressure transducer. In addition to the malfunction of the logger a few times during a spate of about 2.5 m^3s^{-1} on 4 September 2009, the logger at the felled site (site 2) was washed away; therefore, little data are available for this site. In April 2010, a new and more representative felled site (site 3, see *Figure 4.1*) was identified for continuous sampling and data logging, with the guidance and permission of the RSPB. A gauge board and a SEBA MDS Dipper-T3 data logger *(Figure 4.9c)* with a pressure transducer and a temperature sensor were installed at this newly chosen felled site.

(a)

(b)

(c)

Figure 4.9: Automatic stage data loggers calibrated to stage boards, and installed in still wells at (a) intact site, (b) forested site, and (c) felled site.

The forested site has a continuous record of stage level and temperature data from June 2009 – April 2011, while the intact site has a data gap of ~ 35% for the same period. Similarly, the felled site has a continuous record of stage level and temperature until April 2011, except for May, June and part of July 2010, representing about 30% loss when the logger failed to record any data.

4.6.2. Stream Discharge

In this study, discharge has been calculated from flow velocity measurements which were carried out at each site over a range of flow conditions (Carter and Davidian, 1989; Turnipseed and Sauer, 2010), using a Valeport Open Channel Flow meter (Model 001). The detection range, accuracy and calibration used are provided in *Appendix II.* Details of location, dates, velocity and area measurement procedure, and the resulting discharge calculations, are provided in *Appendix II***.** Estimated discharge values are then compared to the corresponding stage levels to define a rating curve (See *Appendix II*) for each site that can be used to calculate a continuous discharge record using the corresponding stage level data. At the felled site (site 3 in *Figure 4.1*), velocity measurements were not very satisfactory since the stream course was always unstable, therefore unsuitable for flow measurements (Turnipseed and Sauer, 2010). However, the data from the forested site were used to develop a continuous record for this site.

To estimate discharge at an ungauged site, for example at the River Dyke Bridge site (see *Figure 4.1*), it was assumed that the discharge time series at forested site was similar to that at the ungauged site, since these two sites were not very far apart (~ 6.5 km). Hence, the discharge at an ungauged site can be calculated from the flow at the forested site weighted by catchment area, using the following equation *(Eq. 4.1)*:

$$\frac{Flow_{ungauged}}{Area_{ungauged}} = \frac{Flow_{gauged}}{Area_{gauged}}$$

(Eq. 4.1)

For the intact site, missing data gaps were filled by correlating the stage level data rather than the discharge at the forested site. This was done since the slope of the area, and the discharges differ between these two catchments. Although this method is undoubtedly an over-simplification of predicting flow at the intact site, it seems acceptable as the general runoff trends are well captured by the calculated data for the intact site and since the relative changes are important rather than the absolute values for this study. Therefore, these calculations were found to be sufficient for the purpose of this study.

Chapter 5
STREAM WATER CHEMISTRY

This chapter presents the data and results of the stream water sampling. General stream water chemistry in the catchment and the effects of landuse practices on water quality are discussed.

5.1. Introduction

Many chemical species are exported into the stream channels in dissolved forms, and they play important roles in many physical, chemical and biological processes of aquatic ecosystems (Allan and Castillo, 2007). However, excessive or depleted concentrations of some of these species can influence the aquatic environments and climate. In upland catchments, significant changes in stream chemistry occur during storm events, as hydrological pathways change. Consequently, dilution of water from base-rich groundwater sources or from B/C horizons by surface and shallow subsurface runoff through organic-rich layers of soils is generally seen (Billett and Cresser, 1996; Soulsby *et al.*, 1998; Jarvie *et al.*, 2001; Miller *et al.*, 2001; Abesser *et al.*, 2006b). Therefore, a better understanding of dissolved species concentration variability in stream waters, and the underlying mechanisms affecting their dynamics, is therefore relevant to establishing a conceptual model of the hydrochemical responses of a catchment. This study primarily focuses on the landuse change effects on the streamwater chemistry in the River Dyke catchment.

5.2. Sampling design and methods

Background of the study area, selection of sites and monitoring parameters are provided in Chapters 3 & 4. Stream water samples were collected from five sites in the River Dyke catchment: an intact blanket bog, a

forested site, two felled sites and a site close to the outlet of the catchment *(Figure 5.1)*. Occasional sampling was also carried out at four sites on the main stem of the River Halladale *(Figure 3.1)*. The main objectives for each site and the chosen sampling frequency were to monitor background levels of the stream water chemistry in the River Dyke, and to investigate the spatial and temporal variability in water quality, particularly during storm events (see Chapter 4). In this chapter, the focus is the variability in stream chemistry in relation to different landuse treatments, and data from the main monitoring sites (the intact, forested and felled sites, see *Figure 5.1)* are used to examine those differences.

Sampling periods were spread throughout the year to cover storm events during different seasons of the year whenever possible. Storm event sampling was carried out between August 2009 and April 2011. An initial intensive sampling programme was undertaken between 1 August 2009 and 27 August 2009; other intensive sampling programmes were undertaken in April, July, August, September and November of 2010. Spot sampling was conducted in January, February and March 2011, and a final intensive sampling programme was undertaken in April 2011 (see *Table 4.2*). Usually, a 2-hourly sampling frequency was adopted during the storm events, and 6 and 12 hourly intervals during non-events or when there was no significant change in the flow observed. These intervals were chosen to balance the need for adequate samples that characterise the variability in stream chemistry, against the practicalities of processing and analysing vast amounts of samples. Details of sampling strategies and methodologies, analysis are provided in Chapter 4. A summary of the sites and the data collected are provided in *Tables 4.1, 4.2* and *5.1*. Sampling periods are shown in *Figure 5.2*.

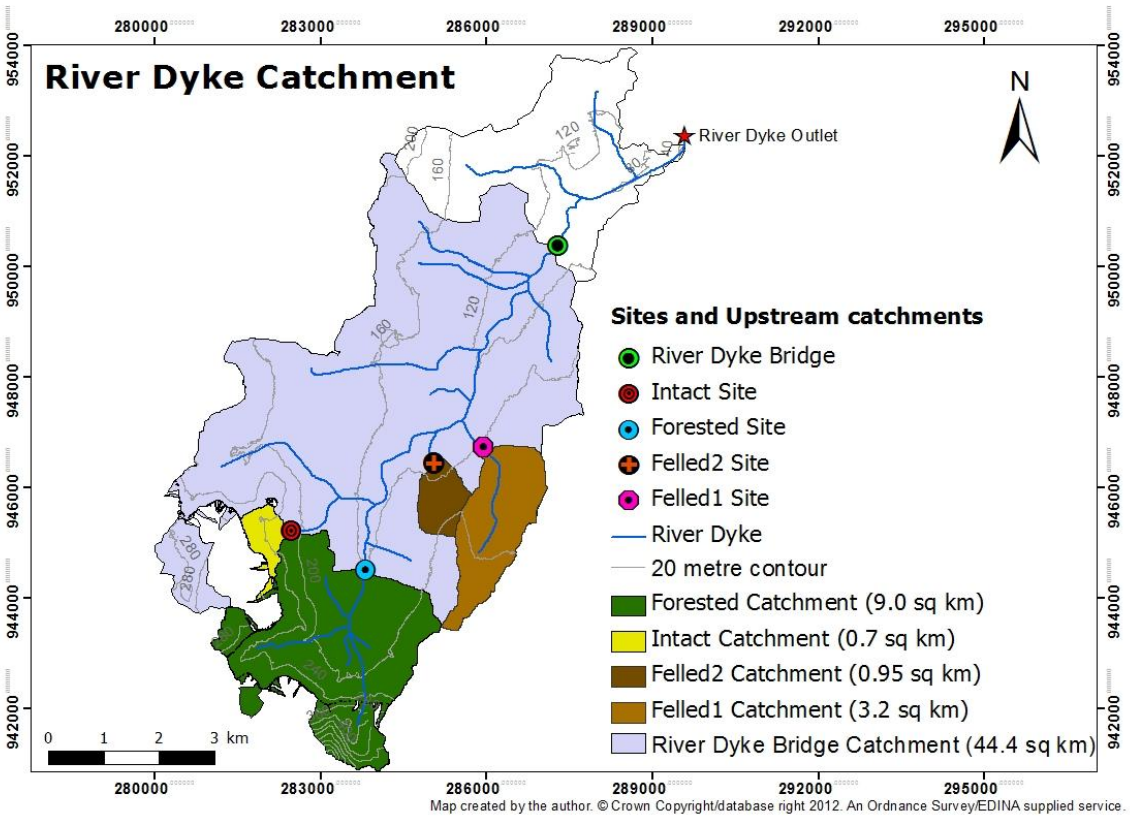


Figure 5.1: Map showing monitoring sites in the River Dyke catchment

5.3. Stream chemistry: Spatial and Temporal variability

Usually, under steady flow conditions and over short time scales, stream water chemistry is presumed to be relatively stable. However, studies have reported that parameters like dissolved organic carbon, trace metals, and base cations vary considerably over shorter time scales and even diurnally due to chemical, physical and biological processes in operation (Kaplan and Bott, 1982; Dawson *et al.*, 2001; Nimick *et al.*, 2003; Spencer *et al.*, 2007). In the present study, stream water chemistry shows spatial and temporal trends and is best illustrated by assessing changes in pH, conductivity, dissolved oxygen (DO), base cations, DOC, metal ions in relation to changing discharge at individual sites as shown in *Figure 5.3 - Figure 5.8*.

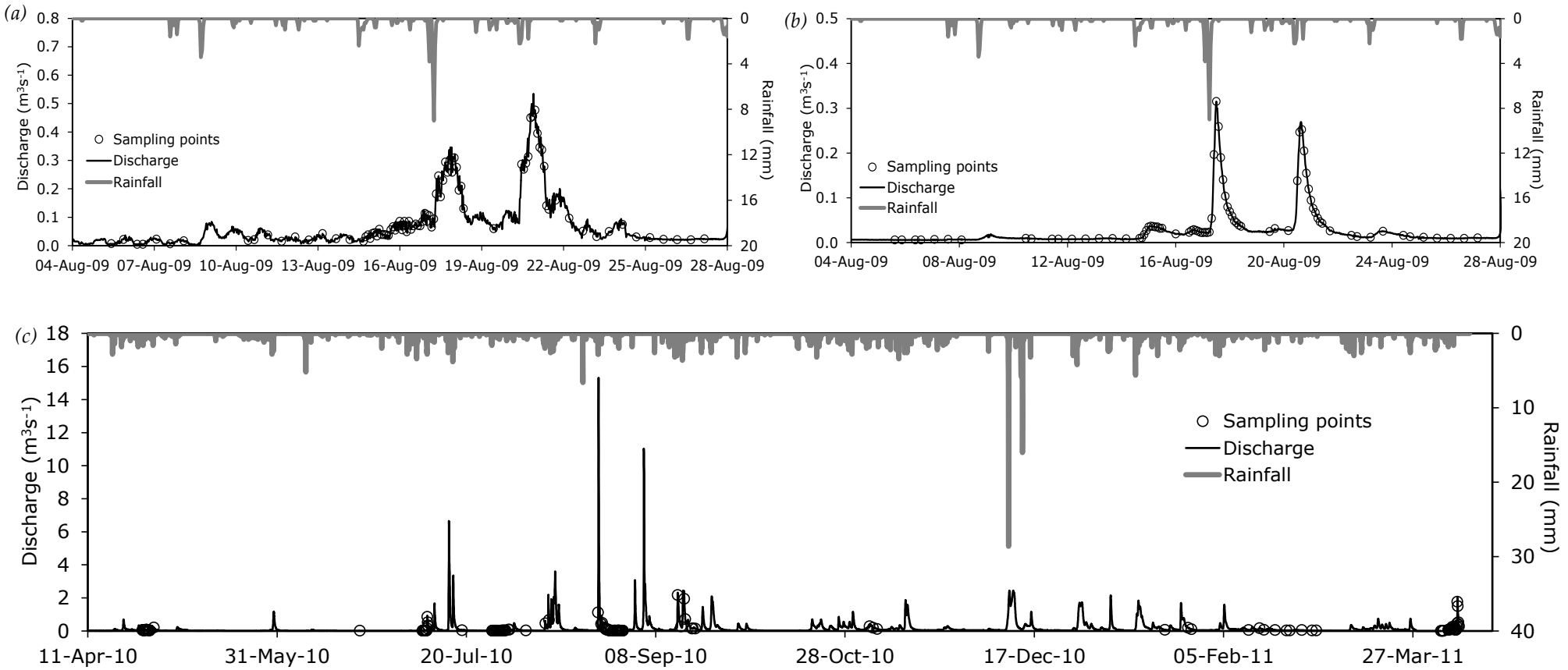


Figure 5.2: Plots showing sampling times, stream discharge and rainfall at all the main monitoring sites: a) Intact site (2009), b) Forested & Felled sites (2009), and c) All sites (2010 & 2011)

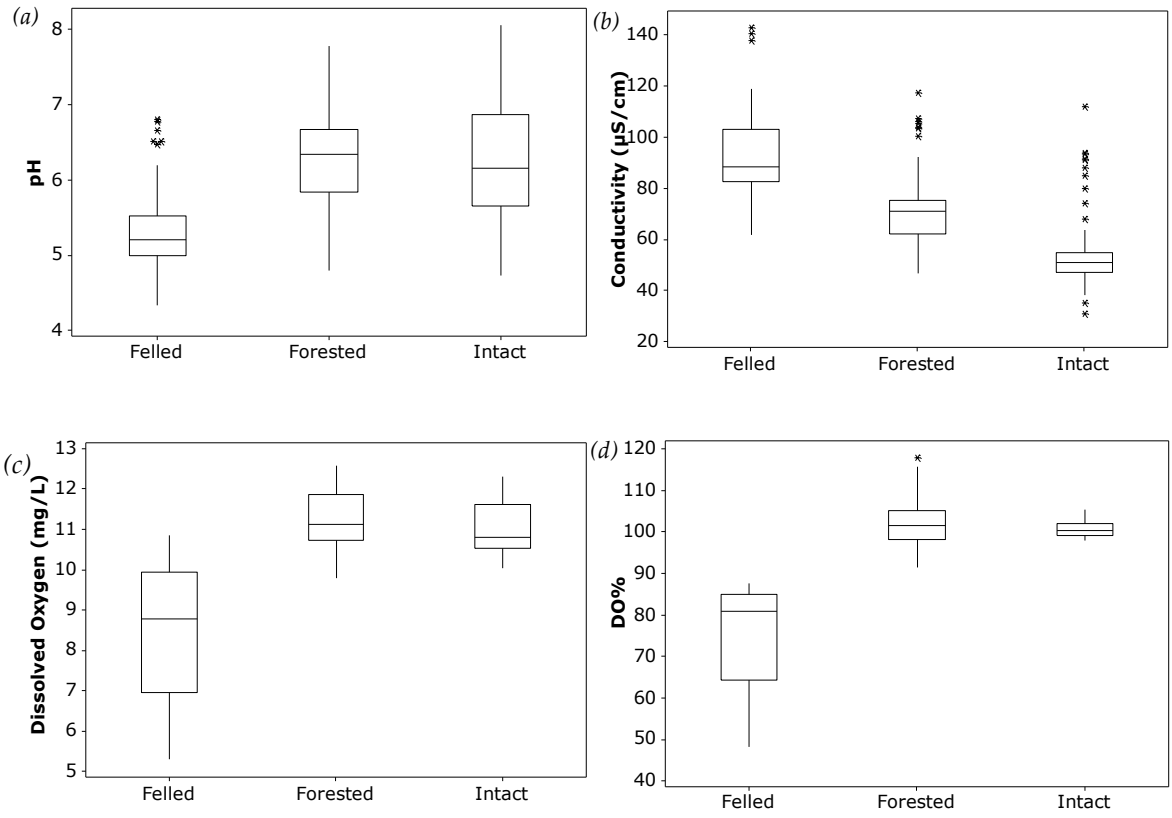


*Figure 5.3: Box plots showing minimum, maximum and median concentrations of: a) pH, b) conductivity, c) & d) dissolved oxygen, for the sites. Whiskers show minimum and maximum concentrations; median concentrations - horizontal line in the boxes; outliers (shown as *) are observations > 1.5 standard deviations.*

Table 5.1 lists the minimum, maximum and mean values for all measured streamwater solute concentrations in the sub-catchments. Mean pH varies from 5.4 in the felled catchment to 6.4 in the forested, typical of upland catchments (Billett and Cresser, 1996). The data show that of all sites, stream waters draining intact peat have the least conductivity values (minimum 30.9 μScm^{-1}) and a maximum pH of up to 8.1 *(*see *Figure 5.3)*. In contrast, lowest pH and highest conductivity values (maximum 142.7 $\mu S\ cm^{-1}$) are recorded in the felled catchment, while intermediate values of these parameters are measured in the forested catchment *(Table 5.1)*.

In the intact site, mean concentrations of Ca (2.0 mg L^{-1}), Mg (1.2 mg L^{-1}), Na (6.0 mg L^{-1}), K (0.4 mg L^{-1}) and Si (153.5 mg L^{-1}) in stream water are low compared to that of the other sites *(Table 5.1)*. In contrast, the concentrations of

these ions are relatively high in the felled site with mean concentrations of Ca (3.6 mg L^{-1}), Mg (2.3 mg L^{-1}), Na (11 mg L^{-1}), K (1.0 mg L^{-1}) and Si (806 mg L^{-1}). Again, stream water samples from the forested site show intermediate concentrations with mean concentrations of Ca (2.8 mg L^{-1}), Mg (1.5 mg L^{-1}), Na (7.1 mg L^{-1}), K (0.45 mg L^{-1}) and Si (271 mg L^{-1}). Of all base cations, Na concentrations are generally higher compared to the other ions in all three sites *(Figure 5.6)*.

Variations in DOC and metal loadings show clear spatial patterns in the River Dyke catchment *(Figure 5.5 & Table 5.1)*. Stream water chemistry at the felled site is low in pH, high in conductivity and base cation concentrations, and is characterised by high loadings and wide ranges in DOC and metal concentrations *(Figure 5.5)*.

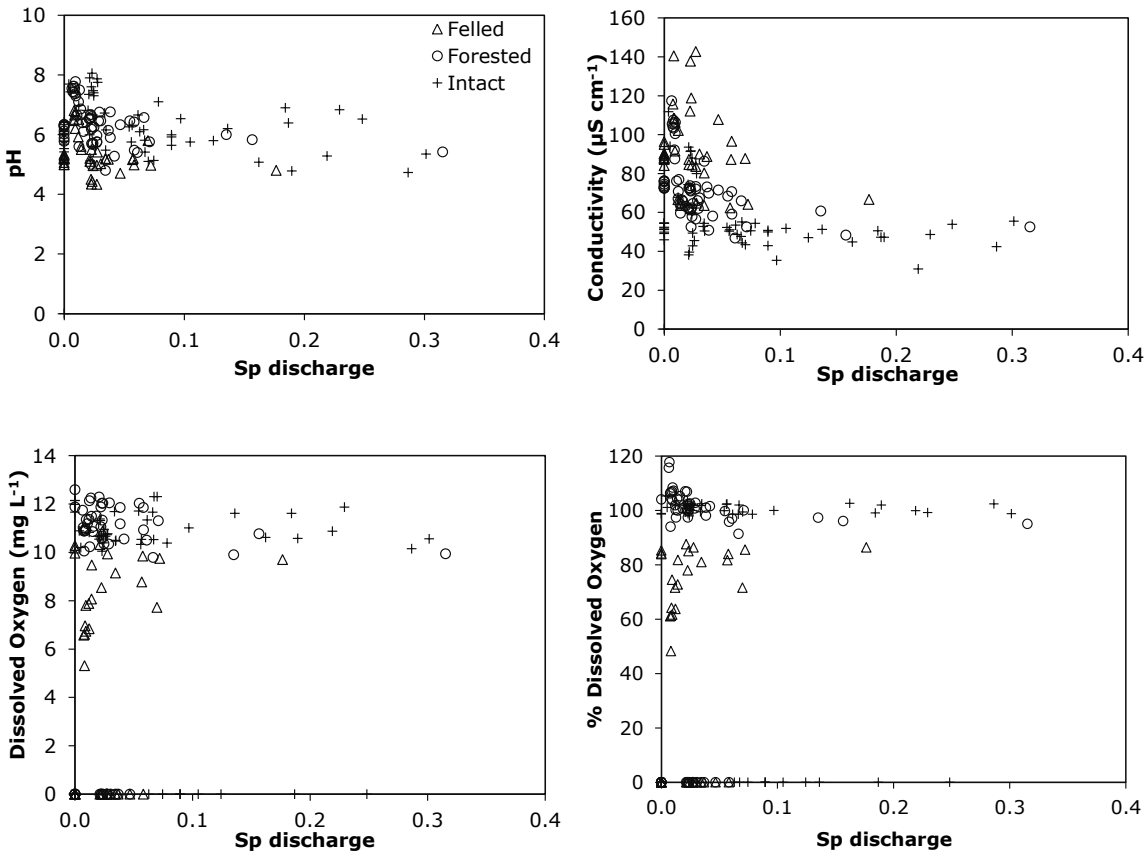


Figure 5.4: Plots showing specific discharge relation to: a) pH, b) Conductivity, c) Dissolved oxygen, and d) % Dissolved oxygen.

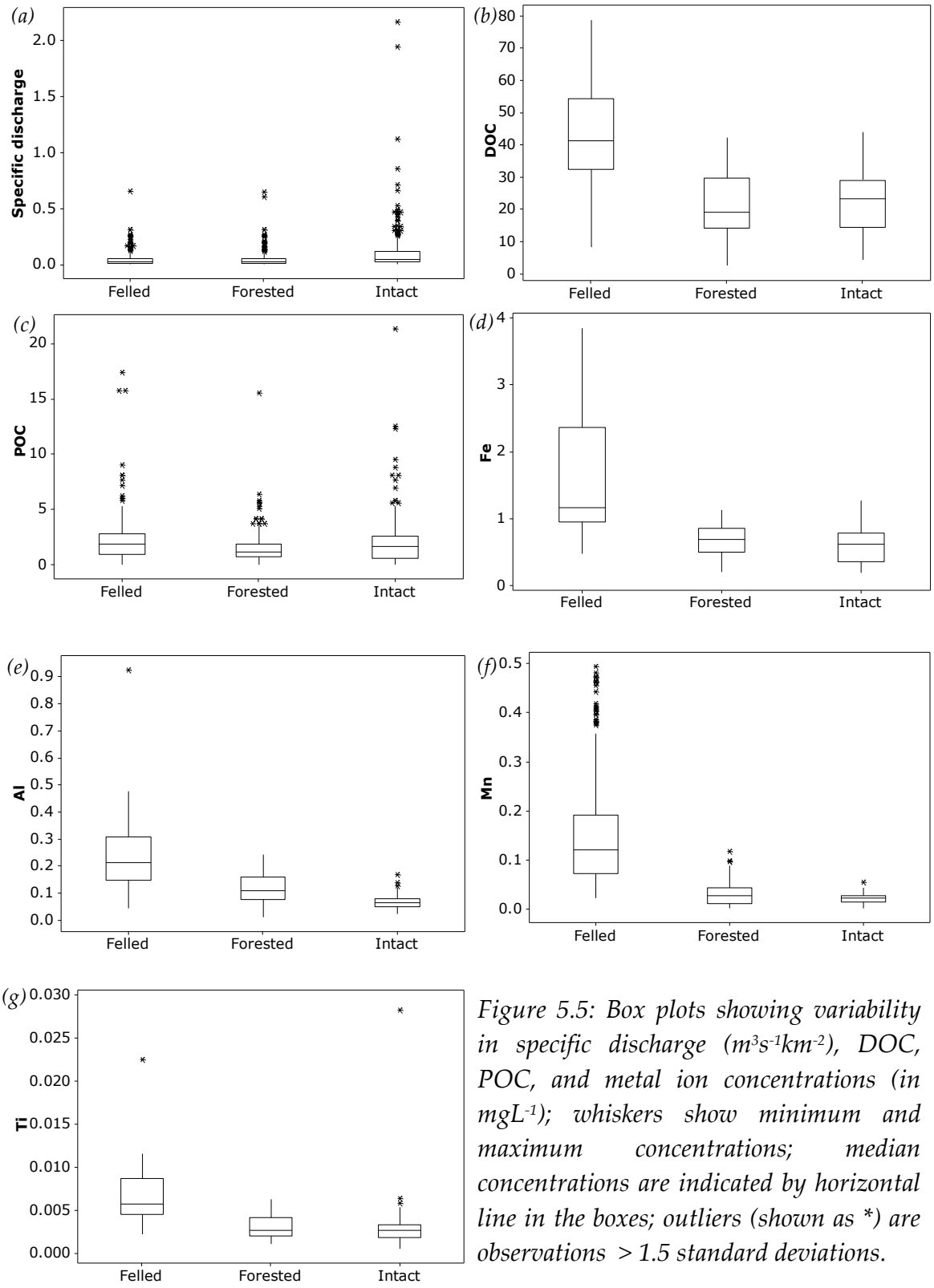


*Figure 5.5: Box plots showing variability in specific discharge ($m^3s^{-1}km^{-2}$), DOC, POC, and metal ion concentrations (in mgL^{-1}); whiskers show minimum and maximum concentrations; median concentrations are indicated by horizontal line in the boxes; outliers (shown as *) are observations > 1.5 standard deviations.*

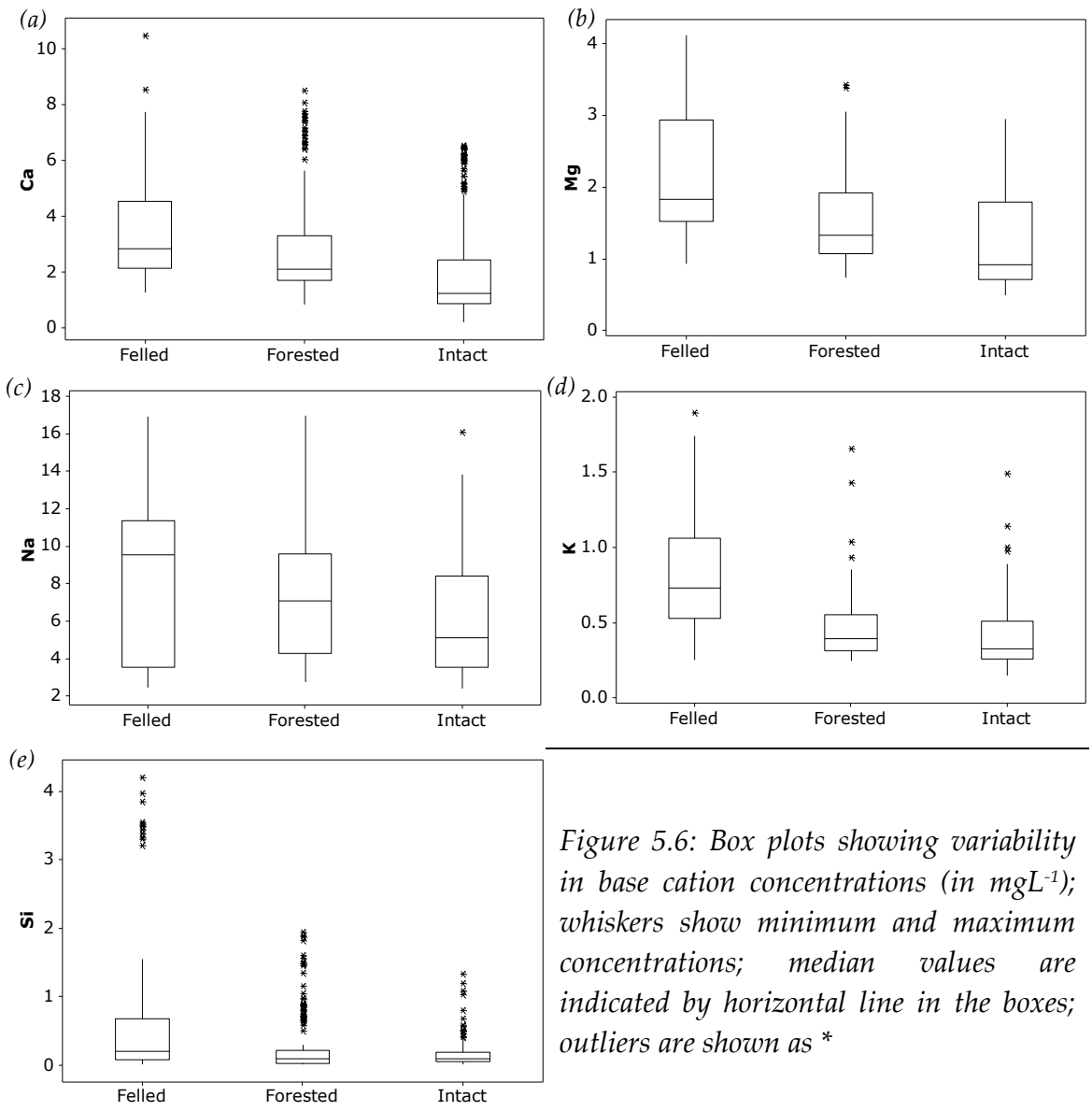


*Figure 5.6: Box plots showing variability in base cation concentrations (in mgL^{-1}); whiskers show minimum and maximum concentrations; median values are indicated by horizontal line in the boxes; outliers are shown as **

Summer DOC concentrations in felled sites are up to 2-3 times higher than those observed at other sites with a maximum DOC of as much as 78.8 mg C L^{-1}. The felled site also exhibits higher mean concentrations of Fe (2.0 mg L^{-1}), Al (285.4 μg L^{-1}), Mn (204.7 μg L^{-1}), Ti (7.5 μg L^{-1}) and Zn (139 μg L^{-1}) relative to the other sites. Uncertainties in these concentrations are provided in *Appendix I*.

		Discharge ($m^3s^{-1}\ km^{-2}$)	*pH*	*Conductivity* (μScm^{-1})	*Dissolved Oxygen* (mgL^{-1})	*Ca* (mgL^{-1})	*Mg* (mgL^{-1})	*Na* (mgL^{-1})	*K* (mgL^{-1})	*Si* (mgL^{-1})	*DOC* (mgL^{-1})	*Fe* (mgL^{-1})	*Al* (μgL^{-1})	*Mn* (μgL^{-1})	*Ti* (μgL^{-1})	*Zn* (μgL^{-1})
	Min	0.005	4.7	30.9	10	0.18	0.50	2.4	0.15	19.3	4.43	0.18	23.7	2.9	0.52	0.35
Intact	Max	2.17	8.1	111.8	12.3	6.53	2.95	16.1	1.49	1324	43.9	1.27	169.2	55	28.3	492
	Mean	*0.12*	*6.3*	*55.9*	*11.0*	*1.99*	*1.19*	*6.03*	*0.39*	*153.5*	*21.2*	*0.6*	*64.8*	*22.3*	*2.7*	*82.4*
	Min	0.01	4.8	46.8	9.8	0.82	0.73	2.76	0.25	5.39	2.52	0.2	12.8	2.75	1.03	4.66
Forested	Max	0.65	7.8	117.4	12.6	8.52	3.42	17	1.66	1942	42.2	1.12	241.4	117.3	6.2	444
	Mean	*0.05*	*6.4*	*72.1*	*11.2*	*2.8*	*1.52*	*7.1*	*0.45*	*271*	*21.2*	*0.68*	*114.8*	*31.8*	*3.1*	*93.9*
	Min	0.01	4.3	61.9	5.3	1.27	0.97	3.4	0.25	10.4	8.2	0.51	117.8	23.5	2.2	24.5
Felled	Max	0.66	6.8	142.7	10.9	10.5	4.11	16.9	1.89	4206	78.8	3.9	923.8	493.4	22.5	551.8
	Mean	*0.05*	*5.4*	*91.1*	*8.6*	*3.56*	*2.29*	*11*	*0.98*	*805.7*	*47.2*	*2.0*	*285.4*	*203.7*	*7.5*	*139*

Table 5.1: Summary of stream water chemistry for individual sites. Discharge displayed is the instantaneous specific discharge ($m^3s^{-1}km^{-2}$) during sample collection; pH, conductivity & dissolved oxygen are normalized to 25^{0}C temperature.

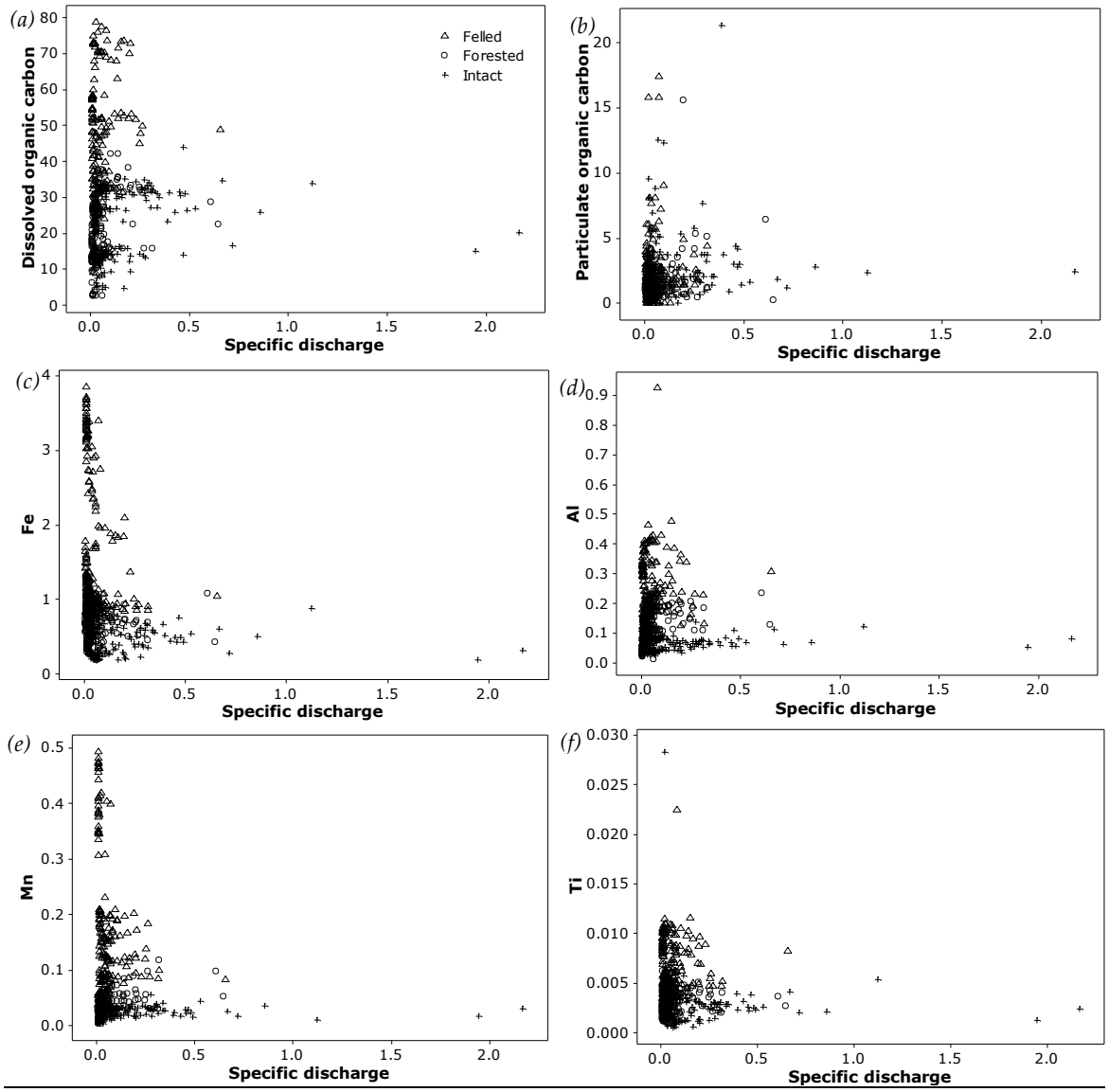


Figure 5.7: Plots showing variability in DOC, POC, Fe, Al, Mn, and Ti concentrations (in mgL^{-1}) related to changing discharge ($m^3s^{-1}km^{-2}$) for the intact, forested and felled sites.

Water chemistry in the intact peat catchment displays low mean DOC (21.19 mgC L^{-1}), Fe (0.58 mg L^{-1}), Al (64.8 µg L^{-1}), Mn (22.31 µg L^{-1}), Ti (2.7 µg L^{-1}) and Zn (82.4 µg L^{-1}) concentrations of all sites *(Table 5.1)*. Mean DOC (21.22 mgC L^{-1}), Fe (0.68 mg L^{-1}), Al (114.8 µg L^{-1}), Mn (31.8 µg L^{-1}), Ti (3.05 µg L^{-1}) and Zn (93.9 µg L^{-1}) concentrations in the forested catchment are generally slightly higher than those observed in the intact site. However, minimum

concentrations of DOC, Al and Mn, and maximum concentrations of DOC, Fe, Ti and Zn concentrations in the forested catchment are slightly lower than that measured in the intact site *(Table 5.1)*.

On comparison, spatial variability in the stream water chemistry of intact peat and forested site appears to be of relatively low magnitude, except for mean Si and Al where the concentrations in the forested site are ~ 50% higher than measured in the intact peat *(Table 5.1).* The felled site shows the highest loadings for all the elements, except for low pH.

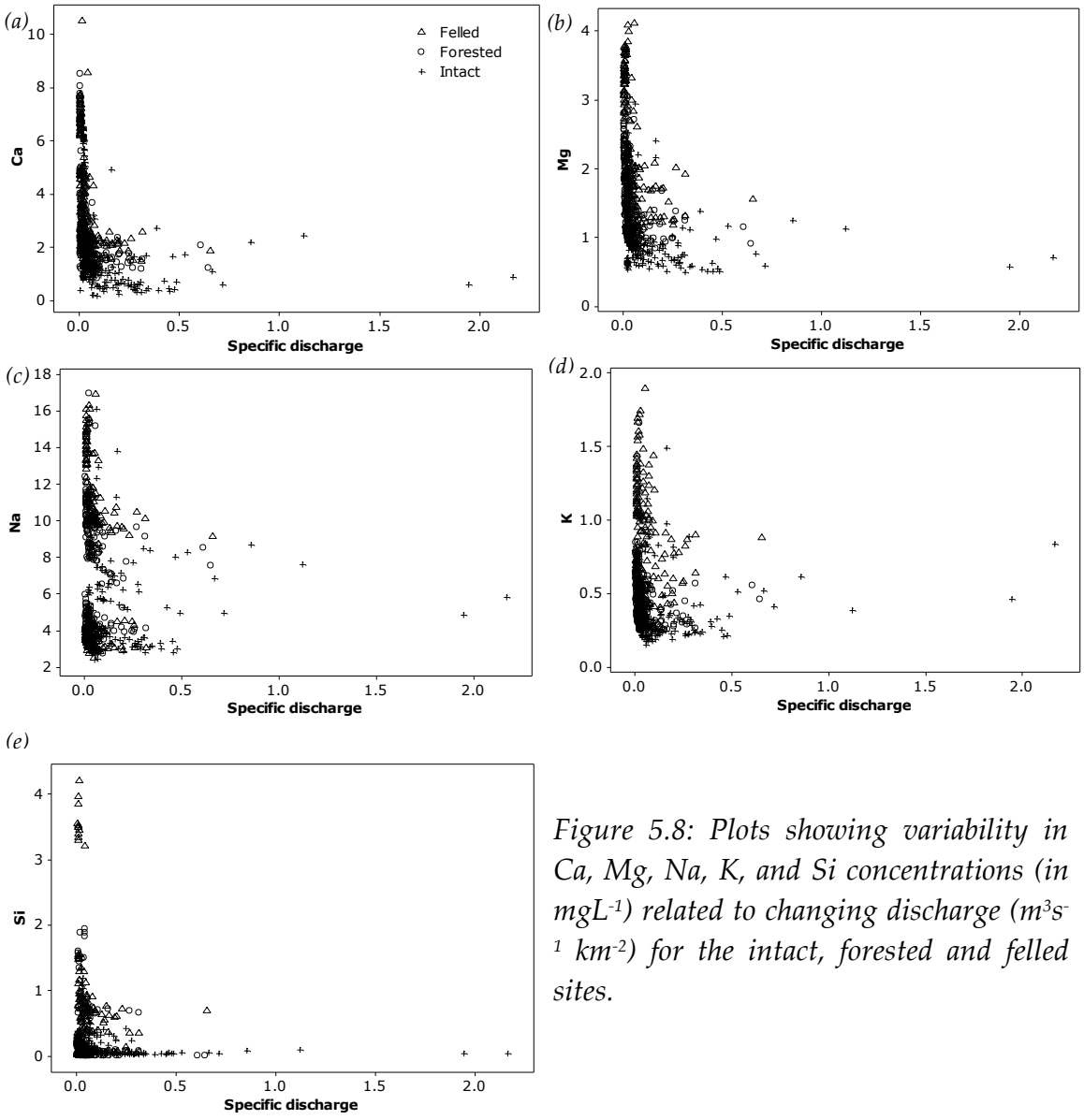


Figure 5.8: Plots showing variability in Ca, Mg, Na, K, and Si concentrations (in mgL^{-1}) related to changing discharge (m^3s^{-1} km^{-2}) for the intact, forested and felled sites.

Variability in pH, conductivity, dissolved oxygen, DOC, metal ion and base cation concentrations related to changing discharge are illustrated in *Figures 5.4, 5.7 & 5.8*. Statistical relationships between discharge and stream water chemical parameters are summarized in *Table 5.2*. In all three sites, pH and conductivity is negatively correlated with flow, however the correlation is weak for conductivity in the felled site. *Figure 5.4a & b* shows that pH and conductivity values in the stream water are highest during low flows, and tend to decrease with increasing flows during storm events. In contrast, dissolved oxygen and percentage dissolved oxygen (DO %) in stream water exhibit a strong positive relationship with discharge in the felled site and correlate negatively in the forested and intact sites; however, the relationship is weak at the intact site *Figure 5.4c & d*.

Calcium (Ca) and magnesium (Mg) concentrations correlate negatively (high) with discharge in all the sites, with the highest correlation coefficients occurring in the forested and felled sites *(Table 5.2a & Figure 5.8).* The other two weathering-derived ions, sodium (Na) and potassium (K) in general show negative correlations with discharge, although the relationships are slightly weaker than that for Ca and Mg, in all three sites. Similarly, Si shows a strong negative and weak negative relationship with flow in the intact and forested sites, respectively, in contrast a weak positive correlation between Si and discharge is seen in the felled site *(Table 5.2a)*.

In the intact site, DOC, Al, and Zn show weak positive relationship with discharge, while the positive correlation of Mn is strong in this site *(Table 5.2b* and *Figure 5.7)*. In this site, Fe, and Ti exhibits negative relationship with flow however, the correlation is weak for Ti. In the forested site, DOC, Al, and Mn show strong positive correlation with discharge whereas, Ti, and Zn show a

similar relationship but relatively weak. Fe shows a weak insignificant relationship with flow in this site *(Table 5.2b* and *Figure 5.7)*. In the felled site, DOC, Fe, Mn, and Ti show inverse relationship with flow, however relatively strong for Mn. Similar to the other two sites, Al, and Zn shows a weak positive correlation with discharge in the felled site *(Table 5.2b* and *Figure 5.7)*. In all three sites, particulate organic carbon (POC) concentrations do not show significant relationship with discharge *(Figure 5.7)*, however, higher concentrations are generally associated with peak discharges during storm events *(Appendix IV)*.

Spatial and temporal patterns of streamwater chemistry in relation to changing discharge patterns during the entire study period are illustrated in *Appendix IV*.

Table 5.2: Spearman rank correlation of streamwater chemical characteristics with discharge for individual sites.

a)	*pH*	*EC*	*Ca*	*Mg*	*Na*	*K*	*Si*
Intact	-0.564[a]	-0.663[a]	-0.578[a]	-0.566[a]	-0.366[a]	-0.268[a]	-0.410[a]
Forested	-0.633[a]	-0.675[a]	-0.698[a]	-0.654[a]	-0.177[c]	-0.509[a]	-0.113[d]
Felled	-0.692[a]	-0.332[d]	-0.736[a]	-0.604[a]	-0.446[a]	-0.339[a]	0.293[b]

b)	*DOC*	*Fe*	*Al*	*Mn*	*Ti*	*Zn*
Intact	0.231[a]	-0.465[a]	0.067[e]	0.590[a]	-0.121[d]	0.071[e]
Forested	0.454[a]	-0.060[e]	0.641[a]	0.681[a]	0.344[a]	0.230[b]
Felled	-0.070[e]	-0.334[a]	0.036[e]	-0.626[a]	-0.036[e]	0.039[e]

[a] $p < 0.001$, [b] $p < 0.005$, [c] $p < 0.01$, [d] $p < 0.1$, and [e] $p > 0.1$

5.4. Discussion and Conclusions

In this study, the results show notable differences between the intact, forested and felled sites in terms of streamwater chemistry. For example, streamwater at the intact site are characterised by low conductivity, low base cation and Si concentrations, while in the forested and felled sites streamwater exhibit intermediate and high concentrations of the above parameters, respectively. High concentrations of these elements in the forested and felled sites are probably due to relatively high amount of underlying glacial till and alluvium (Langan *et al.*, 1995) in these sites (see *Figure 3.3b*). Despite relatively homogenous bedrock geology (*Figure 3.3a*) across the River Dyke catchment, differences in the streamwater chemistry in terms of weathering derived cations, are probably due to the local variations in the bedrock weathering rates (Nezat *et al.*, 2004). However, adjacent streams with similar geology, soils and vegetation may still have different chemistries (Hill and Neal, 1997) which may arise due to small-scale changes in bedrock mineralogy (Reynolds *et al.*, 1986). The felled site is more acidic and high in mean base cation concentrations and conductivity reflecting the effects of disturbance due to felling, and possibly arising due to higher rates of bedrock weathering and cation exchange mechanisms locally.

Streamwater chemistry in the catchment shows a distinct spatial and temporal variability in terms of DOC, and metal ion concentrations (see *Appendix IV*). Mean concentrations of streamwater DOC and metal ions are compared between the sites, at the intact site concentrations are the lowest, while that at the forested site are relatively intermediate and the concentrations at felled site are relatively high (2-3 folds of that at the other sites). Acidic nature and highest mean DOC concentrations in the felled site reflect high organic-rich soil water

inputs even during low-flow periods. Drain-blocking techniques (for restoration) in the felled site makes sure water is stagnant most of the time of the year; such stagnant environments where redox processes are predominant are responsible for the supply of Fe, Mn and other metals to stream waters (Shiller, 1997). High metal ion concentrations in this site are obviously due to higher DOC concentrations, since mobilisation of metals like Fe, Al, Mn and trace metals are principally controlled by the complexation of these ions with DOC (Graham *et al.*, 2002; Tipping *et al.*, 2002; Björkvald *et al.*, 2008; Baken *et al.*, 2011). In acidic conditions, the oxidation of metals like Fe and Mn is relatively slow (Stumm and Morgan, 1996), and metals tend to be more soluble in their reduced forms than in their oxidized forms (Laxen and Chandler, 1983). Therefore, in the intact site, high mean pH could possibly explain the lower metal ion concentrations and similarly, the forested site having relatively intermediate pH and DOC values and hence, intermediate metal ion concentrations.

Response to storm events:

Spatial trends in base cations, pH and conductivity with in the River Dyke catchment are more prominent during low flow periods; however, these trends are evident even during storm events as groundwater can contribute as much as 46% of runoff during events (Jenkins *et al.*, 1994; Soulsby *et al.*, 2005).

During storm events, stream characteristics like pH, conductivity and base cations are largely controlled by stream discharge and hydrological pathways as the concentrations of these elements are highest during low flows when the stream discharge is dominated by contributions from base-rich deep soil or groundwater sources (Jones and Mulholland, 2000; Fitts, 2002). Base cation concentrations in streamwaters in the catchment are found to decrease during

periods of increased runoff. Such a decrease suggests that these elements, which are derived from bedrock weathering processes and dominate baseflow chemistry, are diluted during storm events by more acidic organic rich waters from the surface soil layers (Evans *et al.*, 2008). Temporal variability in Na concentrations does not seem due to precipitation inputs as found in other upland catchment studies (Billett and Cresser, 1996), since no abnormal association of Na peaks with storm events is seen *(Appendix IV)*. In addition, the co-variance of Na with other base cations suggests that Na concentrations are affected by processes like bedrock weathering and/or cation exchange (Soulsby *et al.*, 2005), hence are mainly derived from bedrock weathering. In the intact and forested sites, Si concentrations vary inversely with changing discharge. Therefore, similar to Ca and Mg, the temporal patterns in Si are characteristic of variations associated with the relative contributions of deeper mineral soils and/or groundwater to the discharge *(Appendix IV)*. A positive, however weak, relationship of Si with flow at the felled site probably suggests the removal of excess Si originating from the dissolution of biologically derived silica from the felled trees and/or from the increased weathering due to the soil disturbance (Bailey *et al.*, 2003; Conley *et al.*, 2008) caused as a result of tree-felling. As reported in few studies (Neal *et al.*, 2000; Soulsby *et al.*, 2002), annual variability in silica, due to its uptake by diatoms and benthic algae in summer, is evident for the intact and forested sites, where the concentrations in summer and autumn are relatively higher than those of winter and spring, however it is vice-versa for the felled site suggesting a biological source for Si (Conley *et al.*, 2008).

In the River Dyke catchment, increase in flow during storm events generally decreases pH and conductivity reflecting acidic, base-poor event water (from surface and shallow subsurface) contributions to the stream

discharge (Brown *et al.*, 1999). In all three sites, higher DOC concentrations are generally seen during peak discharges *(Appendix IV)* reflecting the major contribution to stream flow is through shallow organic soils (Billett *et al.*, 2006). Such temporal variations in DOC are usually found to be significant in the upper soil horizons and decline with depth in the soil profile (Lundström, 1993). In general, increase in DOC concentrations coincide with that of Al, Fe Mn and Ti concentrations *(Appendix IV)*, suggesting a close association of metals with DOC (Graham *et al.*, 2002; Abesser *et al.*, 2006a).

The time series graphs shown in *Appendix IV* illustrate that the variability in stream water chemistry in response to discharge fluctuations during storm events is synchronous in all three sites, however, concentrations, magnitude of the changes in concentrations, and the timing of peak concentrations differ between sites. The variability in DOC and metal ion concentrations during storm events is the highest at the felled site compared to the intact and forested sites. In the felled site, during storm events, deeper groundwater sources rich in weathering-derived base cations appear to be significant, as the concentrations are high compared to the other sites despite the high flow contribution of more acidic soilwater. Dissolved oxygen show a strong positive correlation with flow in the felled site and probably indicate the residence time of water before reaching the streams. During intense and long duration, summer storms (*e.g.* August 2009), most of the soil water contribution is from the upper soil layers (Neal *et al.*, 1997; Billett *et al.*, 2006). However, during short duration storm events (*e.g.* July 2010), and during low flow conditions, inputs to streamwater are received from areas adjacent to the stream channel, riparian zones and groundwater , which is reflected in the medium to low DOC and metal concentrations during such periods *(Appendix IV)*.

Table 5.3: Summary table showing qualitative results/differences (in streamwater chemistry) between the sites.

Intact	***Forested***	***Felled***
• In general, stream water is characterised by low conductivity, and low base cation concentrations.	• In general, stream water is characterised by intermediate conductivity, low base cation concentrations.	• In general, stream water is characterised by high conductivity, low base cation concentrations.
• High mean pH => low mean concentrations of DOC and metal ions.	• Intermediate pH => intermediate mean stream DOC and metal ion concentrations.	• Low pH => high mean concentrations of stream DOC and metal ions (2-3 folds of that at the other two sites).
• Si concentrations vary inversely with changing discharge and suggest a source similar to that of Ca and Mg.	• Si concentrations vary inversely with changing discharge and suggest a source similar to that of Ca and Mg.	• A positive, however weak relationship is seen between Si concentrations and stream discharge. Possibility of biological source for Si during summer months is indicated.
• While low flows are dominated by runoff from groundwater sources (rich in base cations), high flows are generally dominated by soilwater runoff (rich in DOC and metal ions).	• Similar to the intact site, high flows are characterised by contributions from soilwater with groundwater dominating the low flows.	• At this site, groundwater is still a significant source of stream water during high flows. • The magnitude of variability in stream water chemistry with changing discharge is relatively the highest.

The findings in this study suggest that spatial variability in stream water chemistry is mainly influenced by catchment characteristics such as bedrock geology, superficial geology, soil type, and landuse. However, the spatial and temporal changes in water chemistry in relation to discharge is a function of hydrologic pathways of water, as the varying concentrations of these elements indicate differences in the residence time of water before reaching the streams.

From the above analysis and discussion, it has been demonstrated that during the events, the main flow pathways switch from deeper sources rich in base cations, to shallower organic soil sources. However, knowledge of how these hydrological pathways vary across different landuse sites, and the hydrological process that are responsible for such changes need to be explored in order to determine the hydrological and hydrochemical responses of each sub-catchment, which will be the focus of subsequent chapters. From the above results, as a first approximation it can be hypothesized that variability in water chemistry is primarily due to the variations in the contribution from two main runoff sources to stream flow and is a two-component mixture. This is based on two main assumptions: i) stream flow at any given point of time is a combination of baseflow and stormflow, and ii) the concentrations of the stream characteristics are mainly controlled by the hydrology of the catchment rather than catchment characteristics such as soils, peat cover and geology. For testing the above hypothesis, a detailed assessment of spatial and temporal variability of stream water chemistry and understanding the pathways followed by water, to reach stream are required. The following chapters will focus on detailed examination of stream water chemistry using statistical techniques to identify streamflow end-members.

Chapter 6
THE UPPER RIVER DYKE CATCHMENT HYDROLOGY

6.1. Introduction

To understand the hydrochemical dynamics in a stream network it is always important to assess the variability in stream chemistry during abrupt changes in discharge associated with storm events, as the flowpaths of water that generate stream flow changes rapidly. Usually, flow paths that dominate during storm events determine the resulting stream water chemistry during and even after the event (Brown *et al.*, 1999a; Abesser *et al.*, 2006b; Worrall *et al.*, 2006a). For example, as soil water contribution increases during a rainfall event, an increase in DOC and associated metal ion concentration is generally seen. Subsequently, as the soil water component reduces and water from deep soils or groundwater sources dominate following a storm event, stream chemistry is characterized by an increase in base cations, pH and conductivity values (Robson *et al.*, 1992; Worrall *et al.*, 2002). Hence, a detail assessment of flow related changes in the stream chemistry is required.

In chapter 5, it has been demonstrated that stream water chemical characteristics such as pH, conductivity, base cations, DOC, and metal ions exhibit distinct spatial and temporal trends. It has been concluded that these changes can be better explained by the hydrological pathways followed by the water to reach the stream channel, residence times of water, and local bedrock weathering rates. In this chapter, factors controlling stream chemistry during storm events are investigated using factor analysis techniques. The primary aim of this chapter is to investigate the contribution of different sources of water to stream discharge generation during storm events. The response of the three

different landuse sub-catchments in the River Dyke catchment are investigated by a) analysing the behaviour of stream water characteristics in each sub-catchment during individual storm events; b) identifying significant factors controlling water chemistry using factor analysis techniques (Q-mode and R-mode); and c) developing an end-member mixing model (EMMA) to estimate the proportion of contributions from different sources to stream flow generation.

From the graphs shown in *Appendix IV*, it is apparent that stream chemistry in all sites shows an abrupt response to individual rainfall events, usually characterised by a sudden drop in pH, conductivity, and base cation concentrations, and a significant increase in DOC and metal ion concentrations. However, for an overview and comparison of trends and relationship among the chemical variables, the results from the stream chemistry analyses are summarised for each site in the form of matrix scatterplots *(Figure 6.1 - 6.3)*. While the graphs highlight that a range of inter-elemental relationships exist, a distinct relationship of some variables with discharge is evident. However, the relationships between the variables are complex making the interpretation of dependencies more difficult by just visual inspection of the scatter plots. To aid analysis between variables and to compare them across the sites, a multivariate *factor analysis* technique has been utilized in order to delineate the different sources of stream flow generation using the hydrochemical signatures characteristic of that particular source.

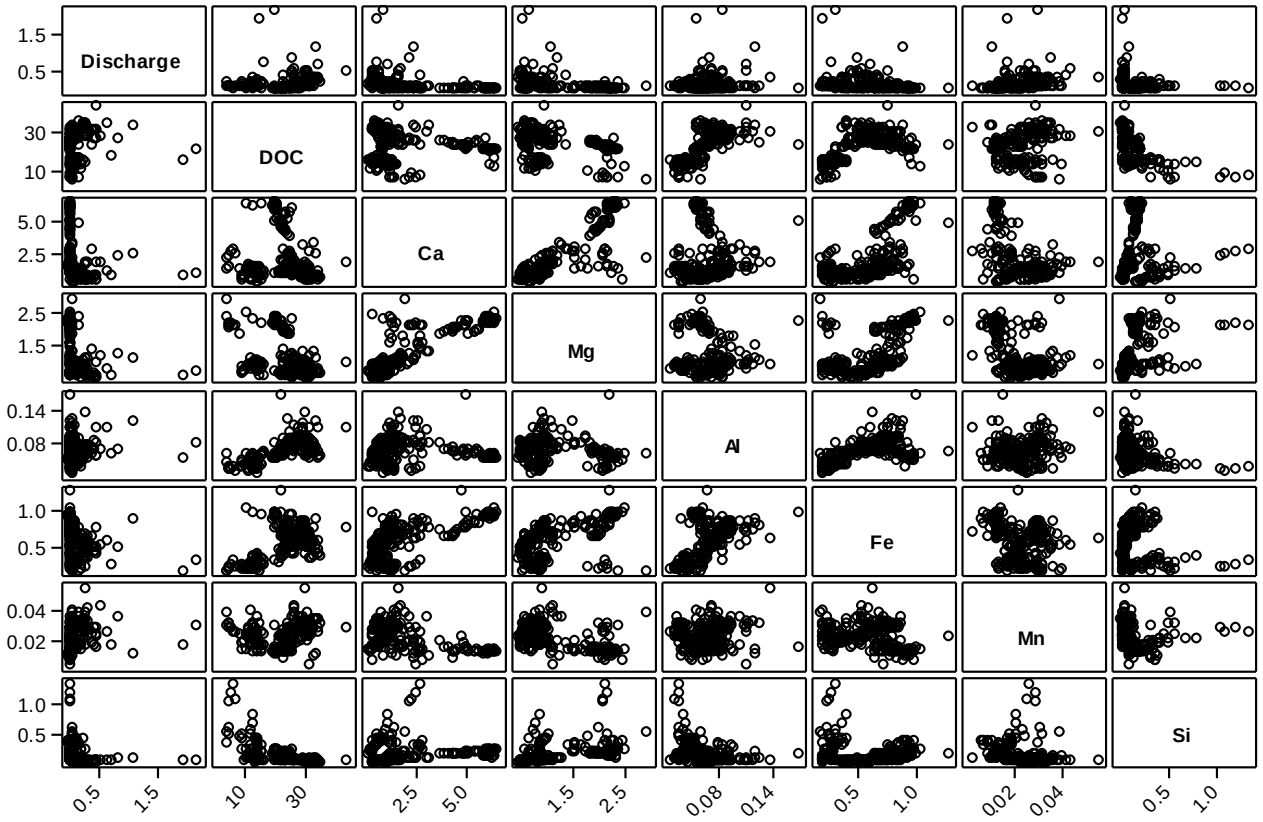


Figure 6.1: Matrix plots showing inter-relationships between discharge, DOC, Ca, Mg, Al, Fe, Mn, and Si in the stream water from the intact site. All measured in mgL^{-1}, except discharge (m^3s^{-1}).

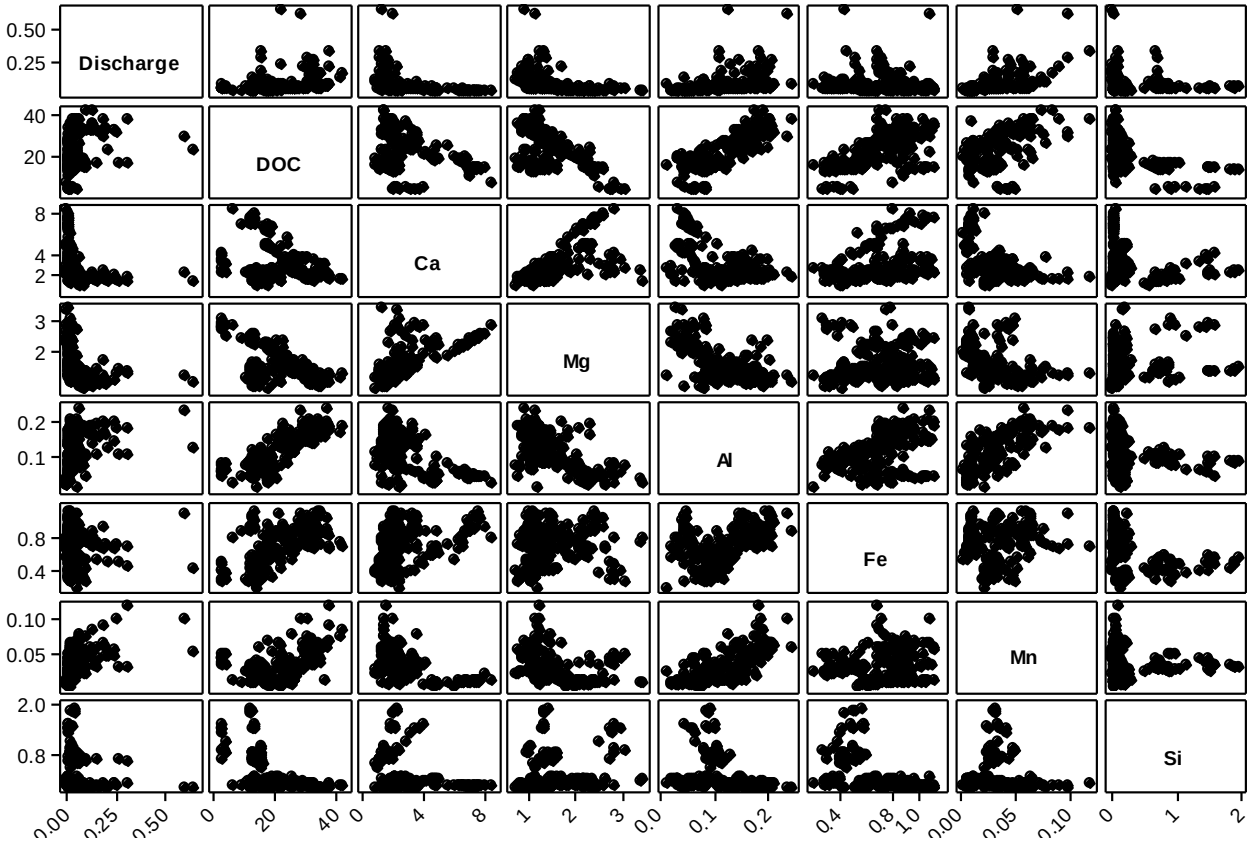


Figure 6.2: Matrix plots showing inter-relationships between discharge, DOC, Ca, Mg, Al, Fe, Mn, and Si in the stream water from the forested site. All measured in mg L^{-1}, except discharge (m^3s^{-1}).

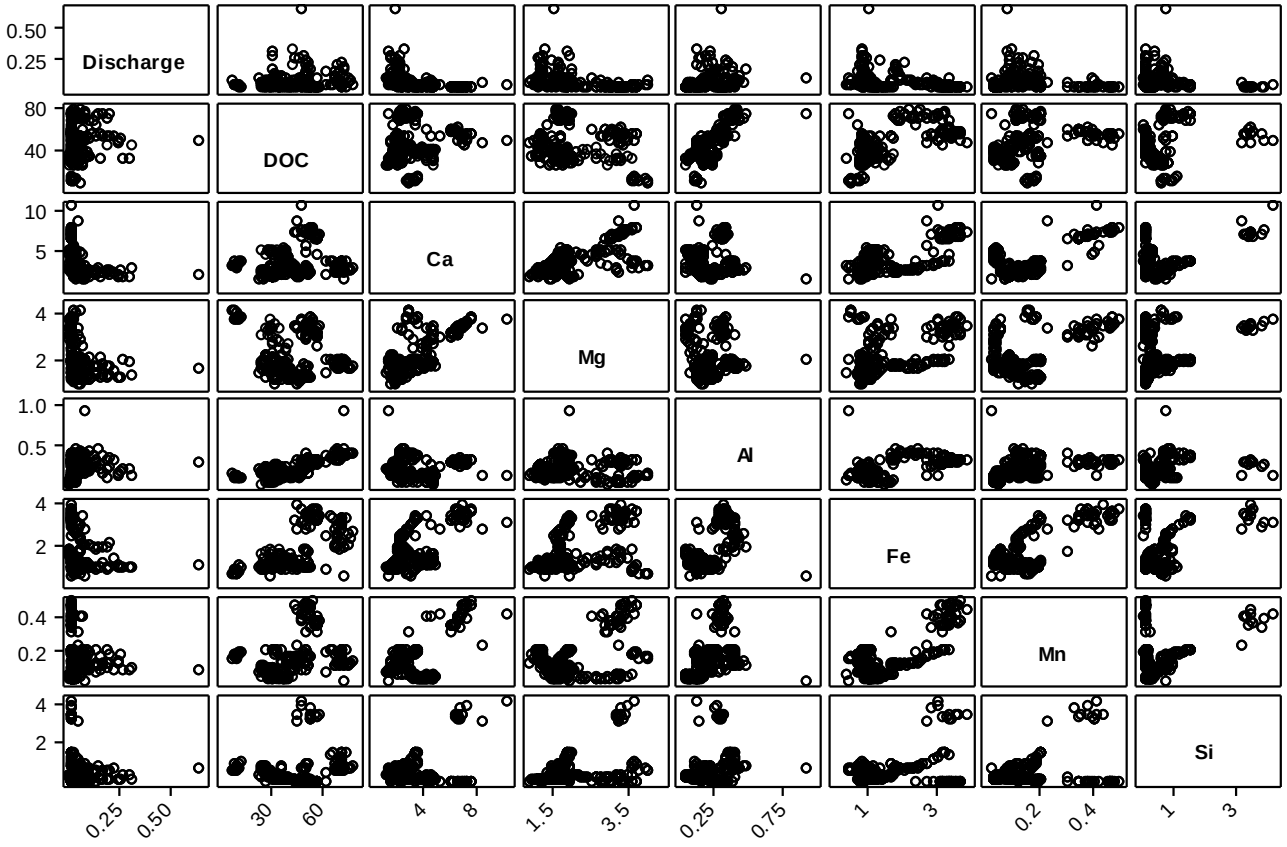


Figure 6.3: Matrix plots showing inter-relationships between discharge, DOC, Ca, Mg, Al, Fe, Mn, and Si in the stream water from the felled site. All measured in mgL^{-1}, except discharge (m^3s^{-1}).

6.2. Factor Analysis

Factor analysis is a widely used multivariate technique for data reduction and is a collection of a number of methods used to examine underlying mutual relationships within a set of measured variables or samples (Davis, 1986; DeCoster, 1998). The primary objective of factor analysis is to reduce the dimensionality of the raw data by analysing the underlying patterns of correlations or covariance in the data. This technique transforms the original variables into a reduced number of mutually uncorrelated, underlying factors and the most significant of these factors account for more variation within the data and occupy a set of mutually orthogonal axes in a 'multi-dimensional' factor space (Kovach, 1995).

Factor analysis has been used successfully in various geological, hydrological, geochemical and environmental studies (Reid *et al.*, 1981; Evans *et al.*, 1996; Wayland *et al.*, 2003; Abesser *et al.*, 2006b) to reduce complexity in large datasets and identify which factors influence stream chemistry within a catchment. Factors produced in this technique are based on eigenvalues derived from a correlation matrix (Davis, 1986; Evans *et al.*, 1996). Factor methods can be grouped into R-mode and Q-mode techniques, both of which can be performed simultaneously or separately. R-mode factor analysis is employed when the primary focus is to understand the inter-correlations among the variables, whereas Q-mode factor analysis, similar to cluster analysis, attempts to find groups of samples (rather than variables) that plot close together in a factor space (Kovach, 1995).

In this study, a simultaneous R-mode and Q mode factor analysis is adopted to identify variables (or samples) which behave in a similar way in the three different sites in the River Dyke catchment, and to relate this to the in-

catchment processes (or landuse) causing such variations. The method follows a procedure proposed by Davis (1986) and Walden and Smith (1995). More detailed discussion of methods and algorithms are provided in these references.

6.2.1. Methods and data analysis

6.2.1.a. Variable selection

The most efficient application of factor analysis is achieved by careful selection of the representative input variables; that is, factors produced by the analysis should be the ones that give the most insight into what controls data co-variance or variability. For example, if a data set contains several variables that belong to the same source or same controls, then all those variables would emerge as the 'principal factor' which leads to a bias (Rogerson, 2011). This could be a limitation when it comes to stream water data as many dissolved species have the same or similar source, and are controlled by a collective factor (discharge). A set of nine parameters (variables) are included in the factor analysis: DOC, Al, Fe, Ti, Mn, Ca, Mg, Na, and K. These species were chosen as they reflect a range of base (rich in Ca, Mg, Na, and K) to storm (DOC, Al, Fe, Mn, and Ti) flow conditions.

6.2.1.b. Data Pre-processing

The raw datasets used for the factor analysis have to meet certain requirements, such as being multivariate and normally distributed, and the number of samples should be larger than the number of variables (Davis, 1986). Normalization is the process of restructuring the data to minimize the potential for anomalies during data processing (Kovach, 1995). Raw data are not necessarily normalized as long as data are not excessively skewed (Child, 2006);

however, data transformation may provide a better ability to interpret factors (Kovach, 1995). Therefore, the raw data were transformed to be close to normal distribution by applying *log transformation* to the data matrix prior to analysis (Cameron, 1996). Once the data are normally distributed, and contain a greater number of samples than variables, the factor analysis requirements are met (Kovach, 1995). As all the variables were measured in same units (mg/L), it was not deemed necessary to standardize the data (Walden and Smith, 1995).

6.2.2. Interpretation of the Results

A simultaneous R-mode and Q-mode factor analysis was carried out on the pre-processed dataset with an aim to extract significant factors that explain the variability in stream water chemistry and aid understanding of the processes responsible for such changes. All R-mode and Q-mode techniques adopted and analyses methods are explained in the *Appendix IV*. Data from all sub-catchments were combined together and factor analysis was run on the pooled data, so that the results for each site could be compared directly. There are certain problems that arise when data are pooled together, such as:

i) landuse is not taken into account and it is presumed that stream flow is generated from, and controlled by, similar sources and processes which may not be true;

ii) despite the sampling frequency being similar at all sites, there are some gaps in sampling at each site due to equipment failure, and this may introduce a bias towards processes occurring in more frequently sampled streams (or hydrological conditions) as they contain larger number of samples.

Therefore, the analysis of the pooled data set will be used only as a basis to identify the main processes controlling stream chemistry, and data from individual sites will account for any local variations.

6.2.2.a. R-mode results – Variable factor loadings

Nine factors were extracted from the rotated factor solution of R-mode analysis on the pooled data set and data from individual sites (*Table 1&2* in *Appendix IV*). The first two factors' eigenvalues were greater than one, and these explain most of the variation in the original data while the other seven factors are element-specific (factors 3, 4 and 5) or are of no significance (factors 6-9). Therefore, factor analysis was re-run to extract only two factors, which was believed appropriate for the purpose of this study. Factor loadings and explained variance are presented in *Table 6.1*.

The eigenvalues for the pooled dataset show that the two factors explain 78% of the variation that exists in the original data set, with factor 1 and factor 2 accounting for 43% and 34% variability, respectively. For the purpose of interpretation, a 'high' loading was defined as greater than 0.7, a significant 'moderate' loading as 0.4 - 0.7, and a loading < 0.4 as 'weak' or insignificant (Evans *et al.*, 1996), although these divisions are arbitrary. From *Table 6.1*, it is evident that DOC, Ti, Al, Fe, and Mn have very high positive (0.76 – 0.95) loadings on factor 1, while Ca, Mg, K and Na have weaker (-0.02 – 0.2) loadings on this factor. In contrast, factor 2 has high positive loadings (0.75 – 0.93) for base cations and weaker (-0.1 – 0.47) correlations for DOC and metal ions. The loadings of the variables on the factors are plotted in the factor space *(Figure 6.4a)* and the plot shows that the nine original variables are clustered into two distinct groups, each of which is characterised by high positive loadings on one of the factors. In the factor space, the degree of correlation between variables in

each group is reflected in how closely they plot relative to each other (*Figure 6.4a)* (Walden and Smith, 1995).

During storm events, and under acidic conditions, DOC forms complexes with metals like Al, Fe, Ti and Mn and removes them in solution (Tipping *et al.*, 2002; Abesser *et al.*, 2006a), and this explains the strong positive loadings of DOC on factor 1 which is associated with stronger loadings of Fe, Al, Ti and Mn. Hence, factor 1 represents soil water source of stream flow generation. In contrast, factor 2 is highly loaded with Mg, Ca, K and Na, which mainly derive from bedrock weathering and therefore this factor represents a groundwater source component. Both factors represent distinct sources of stream flow generation contributing to the flow-related changes in stream chemistry. Thus, results of the pooled data identified two main sources of stream flow generation during storm events.

Factor analysis results for individual sites *(Table 6.1)* show that absolute values of factor loadings and correlations of the variables differ for each site, and factor 1 represents groundwater source in the intact and forested sites but represents soilwater source in the felled site. However, the explained variance values are quite similar for the pooled data and the individual sites, and therefore the change in which factor represents soilwater or groundwater sources can change between the sites. Subsequently, factor analysis results of each individual site were examined to establish site-specific information from the extracted factors. For each site, the first two factors with eigenvalues greater than one are extracted and these explain about 70 - 80% of the variance. Factor loadings for individual sites are listed in *Table 6.1*. In all three sites, factor 1 explains 39% (felled site) to 41% (intact site) of the total variance, while factor 2 explains 31% (forested site) to 38% (intact site) of the variance.

	Pooled data			Intact Site			Forested Site			Felled Site		
Variable	*Factor 1*	*Factor 2*		*Factor 1*	*Factor 2*		*Factor 1*	*Factor 2*		*Factor 1*	*Factor 2*	
DOC	**0.93**	-0.12		-0.27	**-0.89**		-0.39	**0.84**		**0.91**	0.21	
Ti	**0.95**	0.12		-0.02	**-0.95**		-0.34	**0.89**		**0.95**	0.04	
Al	**0.90**	0.19		-0.07	**-0.89**		**-0.64**	**0.59**		**0.85**	-0.14	
Fe	**0.81**	**0.47**		**0.40**	**-0.87**		0.30	**0.90**		**0.73**	**-0.51**	
Mn	**0.76**	0.22		**-0.66**	0.02		**-0.68**	0.15		**0.55**	**-0.56**	
Ca	0.20	**0.81**		**0.87**	-0.27		**0.93**	0.15		0.16	**-0.62**	
Mg	0.15	**0.93**		**0.93**	0.02		**0.90**	-0.15		-0.13	**-0.88**	
Na	-0.02	**0.75**		**0.88**	0.09		**0.47**	-0.12		0.30	**-0.75**	
K	0.20	**0.81**		**0.78**	0.34		**0.67**	-0.30		-0.24	**-0.76**	
			Total			*Total*			*Total*			*Total*
Eigen Values	3.90	3.07	*6.98*	3.67	3.44	*7.11*	3.59	2.83	*6.42*	3.48	2.96	*6.44*
Variance	0.43	0.34	***0.78***	0.41	0.38	***0.79***	0.40	0.31	***0.71***	0.39	0.33	***0.72***

Table 6.1: Factor loading results from R-mode factor analysis for pooled data and individual sites. Factor loadings > 0.4 and < -0.4 are shown in bold to emphasize the significance of the variable on the factor(s).

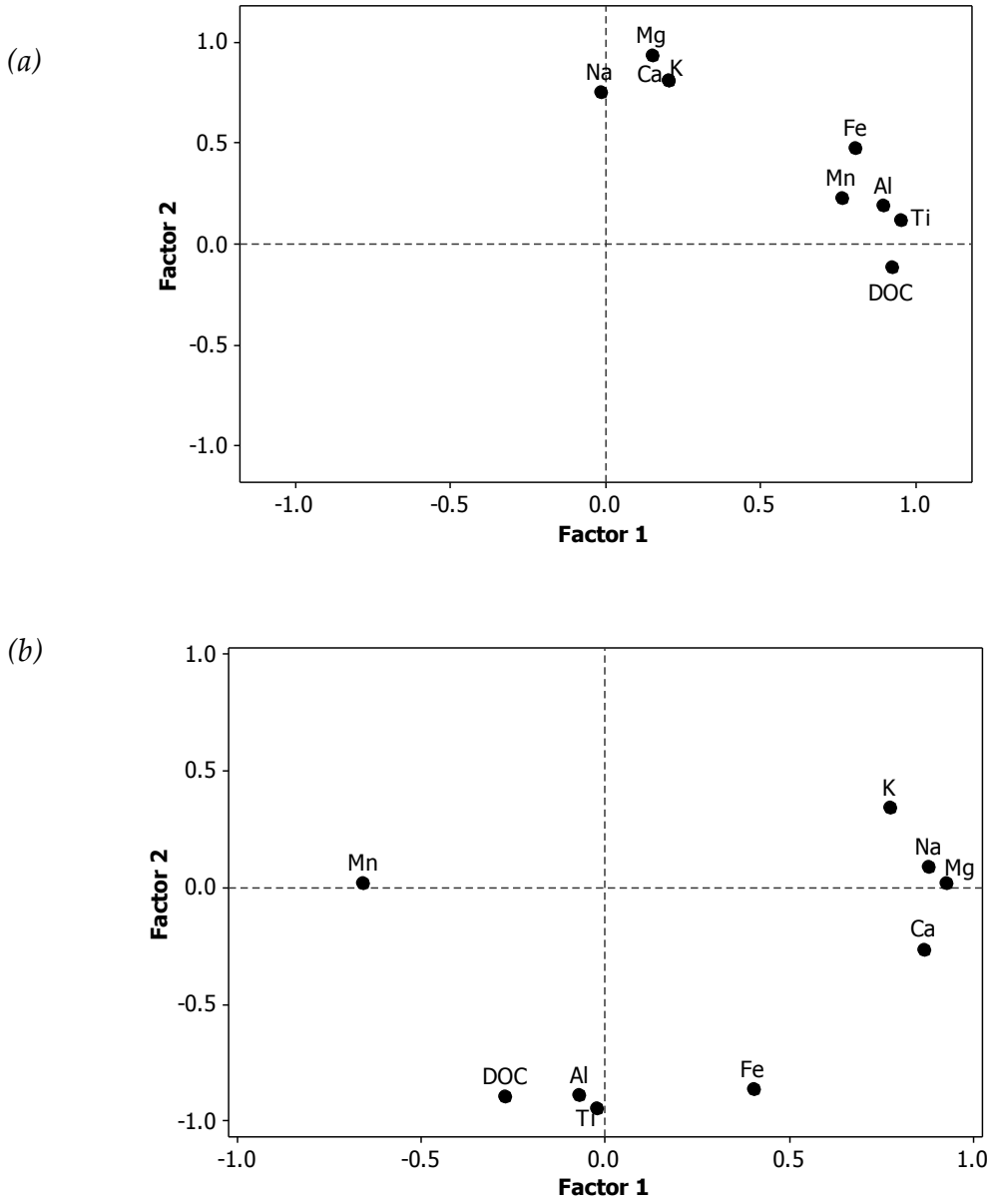


Figure 6.4: Variable factor loadings from R-mode factor analysis plotted on to the factor space derived from : (a) pooled data, and (b) intact site.

In the intact site, weathering-derived base cations (Ca, Mg, Na and K) have strong positive loadings on factor 1. DOC, Ti and Al loadings are weak, and Mn loading is moderate, and all these variables are negatively correlated with base cations. Fe loads positively on factor 1, but not as highly as with

factor 2. Loadings on factor 1 reflect that low flow conditions (high in base cation concentrations) are associated with highly depleted Mn and low concentrations of DOC and other metal ions. Factor 2 has remarkably high negative loadings of DOC, and metal ions (except Mn) and weak positive loadings of base cations, except Ca (weakly negative) *(Table 6.1)*. When plotted in factor space, factor 1 delineates the variables into low flow and high flow groups *(Figure 6.4b)*. Therefore, for the intact site, factor 1 variables are linked to baseflow conditions, and factor 2 and its variables to event flows.

For the forested site, factor 1 has high positive loadings for Ca (0.93), and Mg (0.90), moderate positive loadings for K (0.67) and Na (0.47), and significant negative loadings for Mn (-0.68) and Al (-0.64) *(Table 6.1).* Significant negative loadings of Mn and Al suggest that dissolved forms of these variables increase during high flow conditions, which will buffer base cation depressions (Evans *et al.*, 1996). Loadings of Fe, Ti and DOC are strongly positive on factor 2, while Al loading is moderately positive and Mn is weak. Base cation loadings are insignificant for this factor. Thus in the forested site, factor 1 is representative of groundwater component, while high loadings of variables associated with soil water reflect that factor 2 mainly represents event flow conditions and/or soilwater source. Given the above interpretations, the plot of factor space *(Figure 6.5a)* can be viewed as illustrating that factor 1 delineates the variables into low flow (with positive loadings) and event flow (with negative loadings) groups.

For the felled site, factor 1 has strong positive loadings of DOC (0.91), Ti (0.95), Al (0.85), and Fe (0.73) and a moderate positive loading (0.55) of Mn; base cations loadings are insignificant *(Table 6.1)*. This factor primarily represents high flow conditions where soilwater inputs to streamflow are significant.

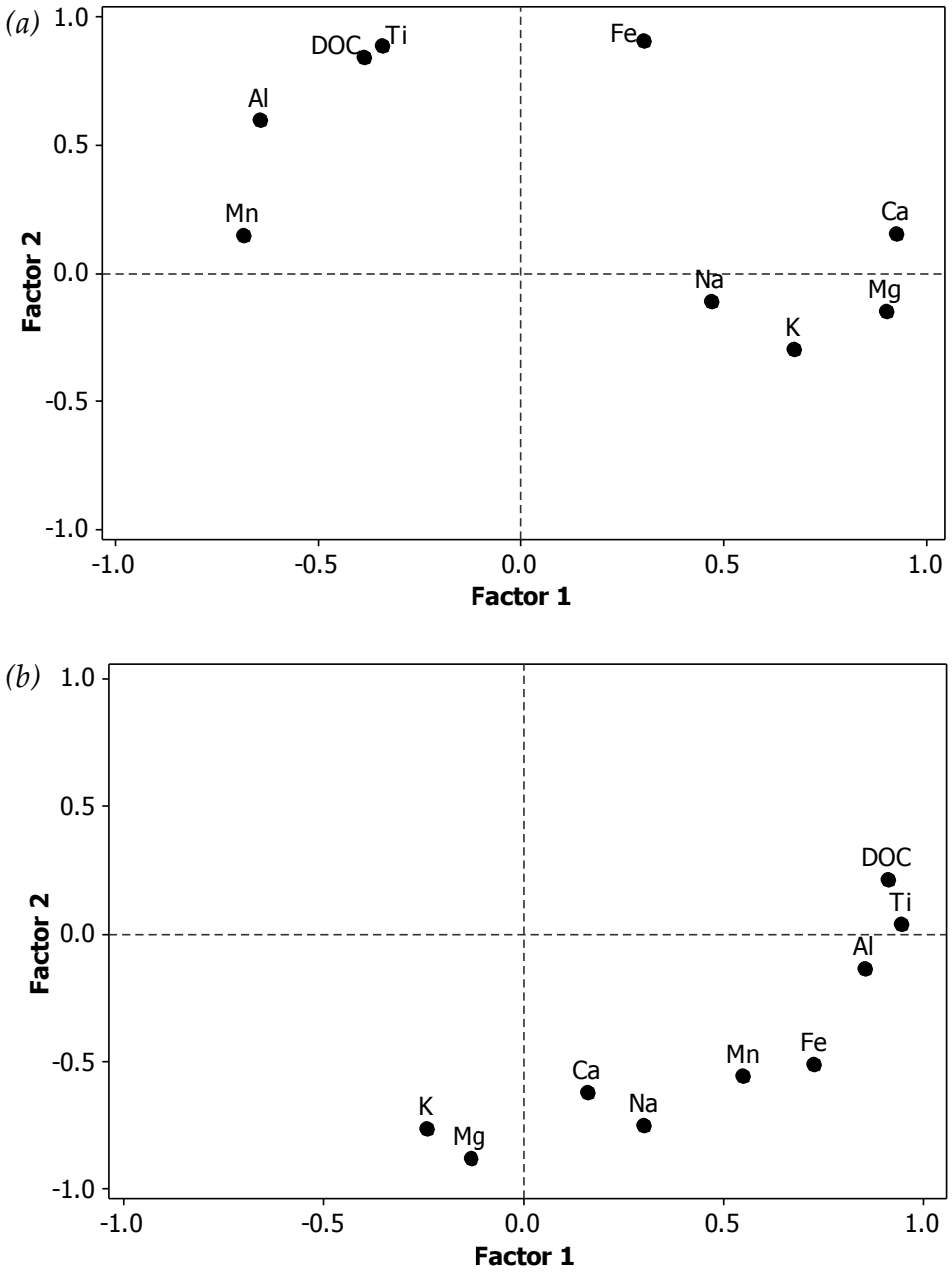


Figure 6.5: Variable factor loadings from R-mode factor analysis plotted on to the factor space derived from : (a) forested site, and (b) felled site.

Factor 2 has strong negative loadings for Mg (-0.88), Na (-0.75), and K (-0.76), moderate negative loading for Ca (-0.62), and moderately negative loadings for Fe (-0.51) and Mn (-0.56); DOC, Ti, Al loadings are insignificant on this factor. Co-occurrence of strong negative loadings of weathering-related

base cations, and significant negative loadings of Fe and Mn, suggest that mobilisation of Fe and Mn in this site may occur in less acidic, deeper mineral soil horizons, as well as upper organic-rich horizons during storm events (Jansen *et al.*, 2003; Abesser *et al.*, 2006a; Abesser and Robinson, 2010), which is consistent with the inverse relationship, however weak, with DOC *(Table 6.1)*. Thus, factor 2 mainly represents the deeper soil and/or groundwater inputs to stream flow. Unlike the other two sites, factor 1 represents a soilwater source at the felled site.

The most notable difference between the felled site, and the forested and intact sites is that the former site's variables do not define as distinct source clusters when plotted in factor space *(Figure 6.5b),* and instead define a curve which gradually shifts from event water chemistries (DOC, Al, and Ti) at one end, through to Fe, Mn, Ca and Na in the middle, and ground water end members K and Mg at the other end. The reason for such a trend in the felled site could be due to the soil structure disturbance caused by tree felling, and the drain blocking (as a part of restoration) measures. Felled tree litter and drain-blocks cuts off rapid runoff during storm events (Holden *et al.*, 2004; Worrall *et al.*, 2007a), which may increase the residence times of water and/or increase groundwater storage, and release the nutrients relatively slowly during storm events (Arnott, 2010).

6.2.2.b. Q-mode results – sample factor loadings

It is evident from the R-mode analysis that the factors and variable loadings are different for each site, which means the samples from all the sites cannot be plotted onto the same factor space. Therefore, the results from Q-mode analysis on the site-specific datasets will be considered for further analysis.

Q-mode analysis on site-specific datasets was used to calculate 'factor scores' of the samples for the two factors that were extracted from the R-mode analysis. The distribution of stream water samples for individual sites is plotted in factor space with the variable (R-mode) loadings *(Figure 6.6)*. It is apparent that sample sets from each of the sites show slightly different ranges of values on factor 1 and factor 2. For the intact site *(Figure 6.6a)*, samples with high positive loadings on factor 1 plot on the far right hand side of the diagram, reflecting relatively high base cation concentrations and/or relatively low Mn levels. Similarly, samples with high negative loadings on factor 1 should plot on the far left hand side of the diagram. Samples with high negative loadings on factor 2 plot on the lower half of the diagram and reflect high DOC and metal ion concentrations (not Mn), and relatively low base cation concentrations (not Ca). Samples with high positive loadings on factor 2, plot in the upper half of the diagram *(Figure 6.6a)*. These relationships are evident in the original data. Hence, samples collected during low flow conditions plot to the right hand side of the diagram *(Figure 6.6a),* and event flow samples plot to the left. This is consistent with the interpretation that factor 1 represents the dilution of base-rich groundwater by more acidic, organic-rich soilwater during storm events.

In the forested site, samples with high positive loadings of base cations that plot to the right hand side of the diagram *(Figure 6.6b)* are enriched in Ca, Mg, K and Na, and are comparatively low in DOC and metal ion concentrations. The explanation for these trends is the same as for the intact site, except that the loadings and scores of factor 2 are reversed in sign *(Figure 6.6a&b)*. Hence, for both the intact and forested sites, factor 1 delineates the streamflow into low flow and high flow, and reflects the dilution of base-rich stream flow chemistry with inputs from soil waters.

In the felled site, samples with high DOC and metal ion concentrations plot to the far right hand side of the plot *(Figure 6.6c)* and are relatively low in base cation concentrations, while the samples enriched in base cations, particularly K and Mg, plot to the extreme left of the diagram *(Figure 6.6c)*. Samples enriched in DOC and Ti are plotted in the far top right hand side of the diagram, suggesting inputs from upper soil horizons. From *Figure 6.6c*, it is evident that factor 1 in the felled site mainly represents a flow-related change from low flow (on the left hand side) to high (event) flow conditions (on the right hand side) in the factor score plot *(Figure 6.6c)*, which is the opposite direction to the other sites.

Stream flow during storm events appears to consist of two main end-members (see *Appendix IV*), as shown in similar studies (Neal *et al.*, 1997; Brown *et al.*, 1999b; Abesser *et al.*, 2006b). From the above analysis, two factors explain about 70-80% of the variance in the data and reflect the stream flow end-members at opposite ends of the x-axis; the effect of mixing of these end-members is depicted by the continuum of the sample data across the two end-members (Neal *et al.*, 1997; Brown *et al.*, 1999b; Abesser *et al.*, 2006b). To further explore these relationships, temporal changes in sample loadings for individual sites are plotted against the changes in stream flow. For this purpose, two series of summer storm events have been selected to illustrate the relationship between factors and the stream flow *(Figure 6.7)*. Given that the two factors represent stream flow contributions from two different runoff sources, these plots also aid in investigating the response of individual sites to particular storm events. From *Figure 6.7*, it is apparent that factor 1 closely relates to groundwater flow in the intact and forested sites, and to soilwater in the felled site, whereas factor 2 is closely related to soilwater flow in the intact and forested sites, and to groundwater in the felled site. Factor loadings related to

soilwater are consistently highest in the forested site, followed by the felled and intact sites. During the first hydrograph event (17 August 2009 - 18 August 2009), the peaks of factor 2 loadings in the intact and forested sites coincide with the discharge peaks. During the second event (20 August 2009 - 21 August 2009), the loadings for the same sites peaked 1 hour and 12 hours after the discharge peak, respectively *(Figure 6.7a&b)*, and a similar pattern is observed during the other events throughout this study. In the felled site, factor 1 (related to soilwater) loadings peaked after 4-5 hours after the hydrograph peak for the same events *(Figure 6.7c)*. These findings are consistent with the peaks of DOC and metal concentrations (mainly derived from soilwater inputs) that are reported in Chapter 5.

Factor loadings related to groundwater increase a few hours before discharge peak, and are followed by a rapid decline at peak discharge, at the intact and forested sites, while a steady increase in the groundwater factor loadings with discharge is evident at the felled site *(Figure 6.7)*. This can be interpreted as the event water in the upper soil layers 'displacing' the deeper water sources into the stream causing an increase in base cation concentrations just before they decline because of dilution by the event water.

Despite the two extracted factors illustrating the changes in hydrological pathways during storm events and increasing influence of soilwater and/or groundwater inputs to stream flow in all the sites, it is apparent that there are different proportions of these sources to stream flow for the different sites, which can explain the differences in concentrations of certain dissolved species. In order to estimate the proportions of different sources to stream flow generation, the factors extracted from the above analysis can be modelled using End-Member Mixing Analysis, where stream chemistry is viewed as a mixture of waters from chemically distinct sources.

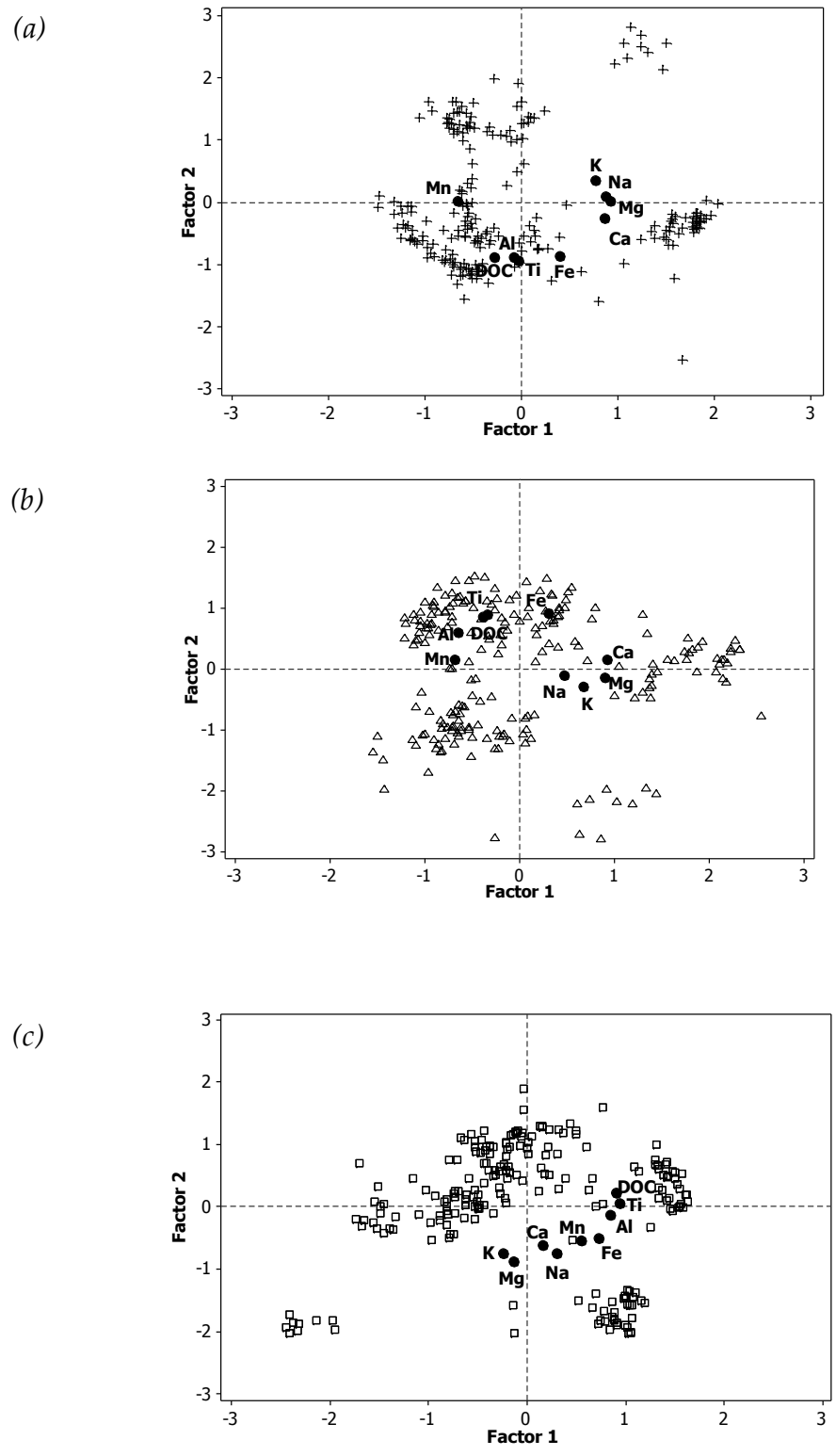


Figure 6.6: Distribution of stream water samples (scores from Q-mode factor analysis) and variable factor loadings in the factor space for individual sites: (a) Intact site, (b) Forested site, and (c) Felled sites.

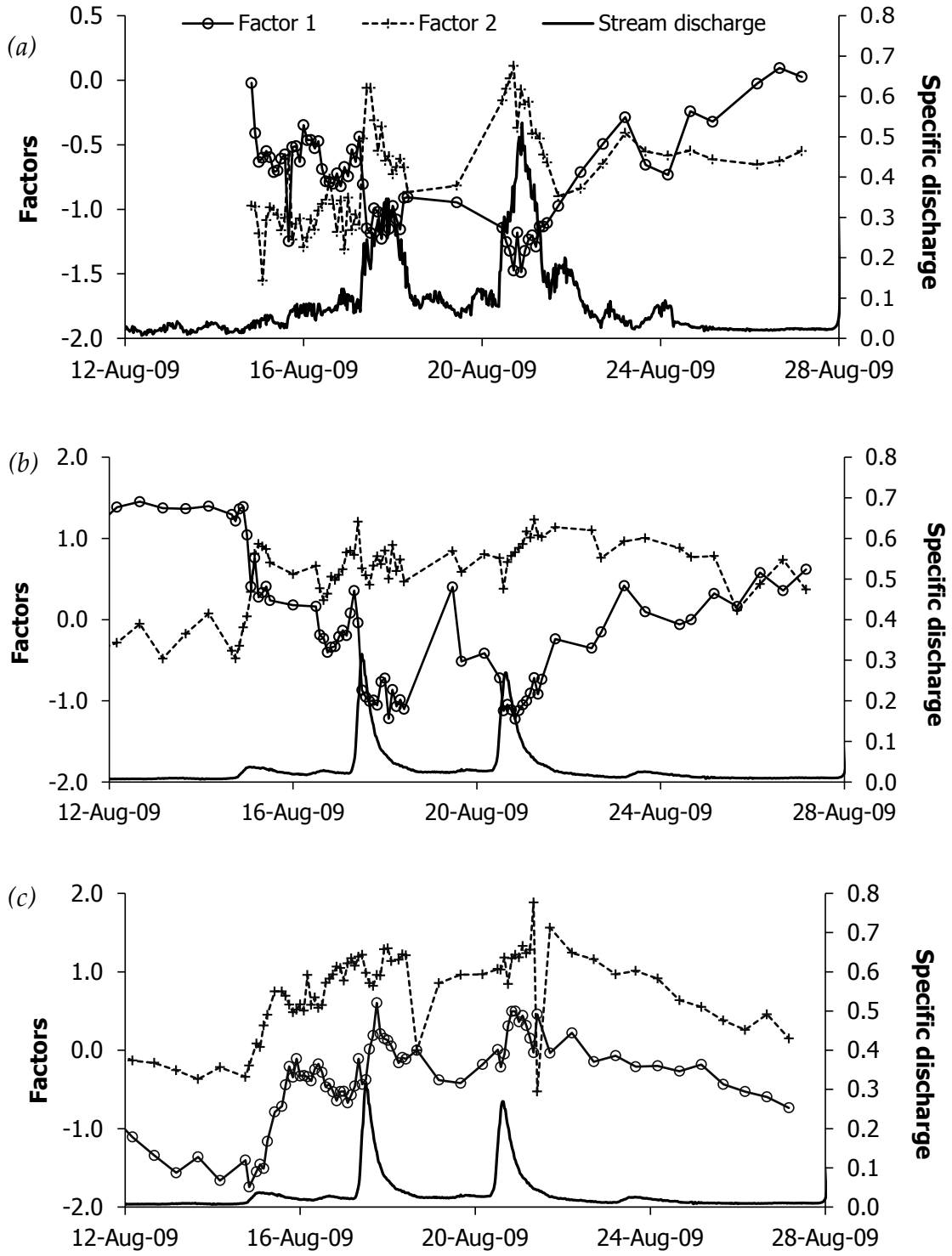


Figure 6.7: Stream water sample loadings on factor 1 and factor 2 during storm events in August 2009: (a) intact, (b) forested, and (c) felled sites. Specific discharge in $m^3s^{-1}km^{-2}$.

Distinct and contrast chemical characteristics of baseflow (base cations) and stormflow (DOC and metals) are evident from the above results, and consequently stream flow can be viewed as consisting of two or more 'end-members' (Hooper *et al.*, 1990). Hence, stream flow during storm events appears to be a mixture of: a) deep ground water component (rich in base cations), b) soil water component (with high Al, Fe and Mn), which also includes near surface flow rich in DOC (Billett *et al.*, 2006; Worrall *et al.*, 2006b).

6.3. Flow duration Curve

The daily mean discharges were computed for each site using the flow record from the sites. The frequencies and cumulative frequencies of occurrence are compiled and were converted into percentages of the total number of days (Gustard *et al.*, 1992; Shaw, 1994; Gustard and Demuth, 2008) to plot a *flow-duration* curve. A flow duration curve, shown in *Figure 6.8*, gives the percentage of time during which a given discharge at a gauging station may be equalled or exceeded (Shaw, 1994).

The comparison of flow-duration curves from the intact, forested and felled sites is shown in *Figure 6.8*. From the plots *(Figure 6.8)*, it can be seen that for 5% (Q_5) of the study period, discharge exceeded 0.6 m^3s^{-1}, 2.67 m^3s^{-1}, and 0.34 m^3s^{-1} at the intact, forested and felled sites, respectively. In addition, for 90% (Q_{90}) of the study period, discharges varied between 0.028 and 0.6 m^3s^{-1} at the intact, 0.2 and 2.7 m^3s^{-1} at the forested and 0.01 and 0.34 m^3s^{-1} at the felled sites. The median values (Q_{50}) shown on the plots provide the average (50% time) discharge values at the sites. These discharge values are very useful for delineating the flows and for choosing the end members for the end-member mixing analysis.

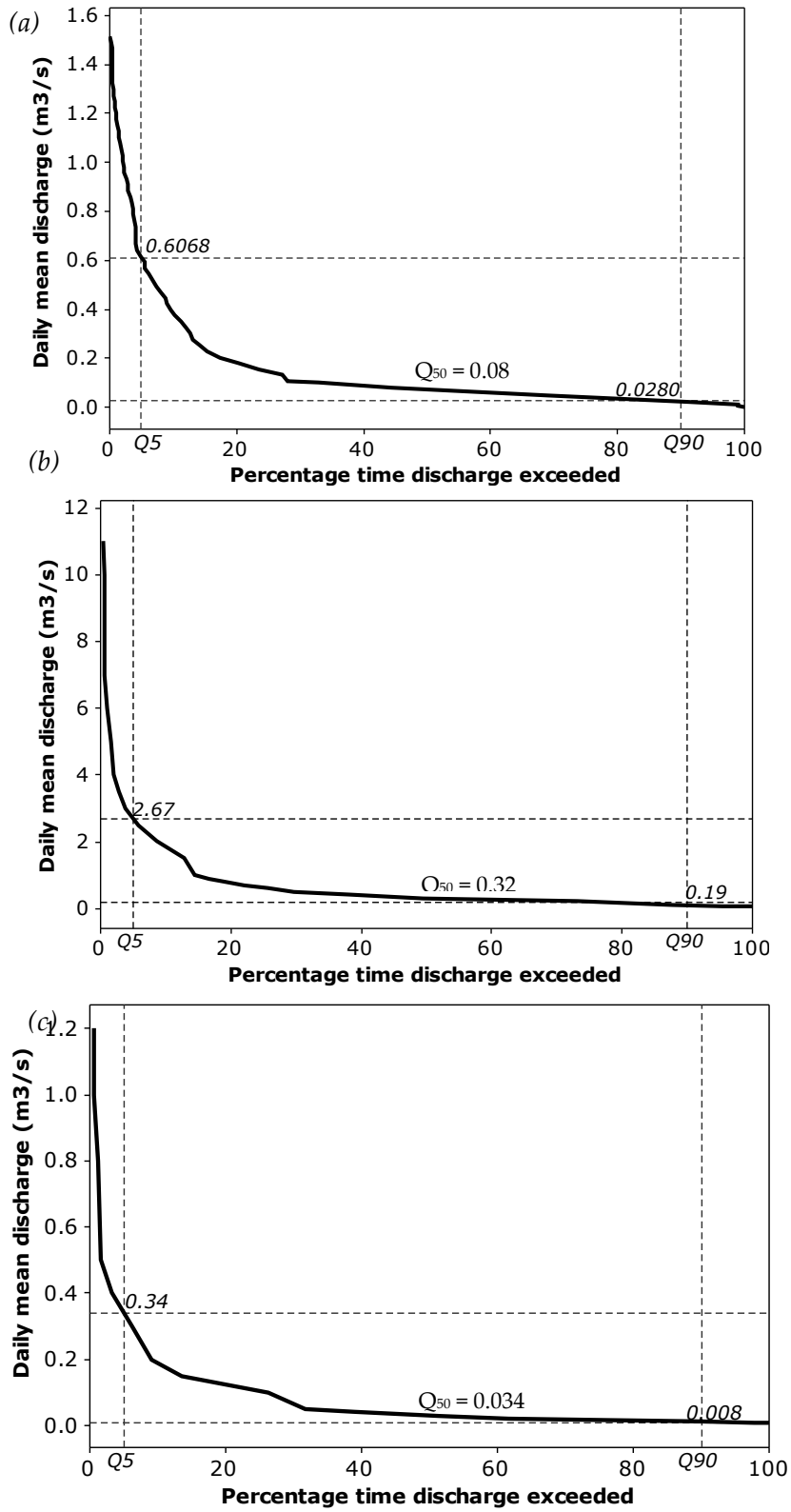


Figure 6.8: Flow duration curves for: (a) intact, (b) forested, and (c) felled sites. Q_5 – high flow, Q_{90} – lowflow, and Q_{50} – median flow values.

6.4. End-member mixing Analysis (EMMA)

In the end-member mixing analysis (EMMA), streamwater chemistry can be analysed as a mixture of chemically defined end-members, which relate to specific soil horizons. This approach is based on the observation that the dissolved species in stream water that most closely correlate with flow are the same ones that display significant variations in concentrations across different soil horizons (Christophersen *et al.*, 1990; Hooper *et al.*, 1990). Hence, EMMA can be used to explore hydrological pathways within a catchment based on the water chemistry of a stream with two or more end members (Soulsby and Dunn, 2003).

One of the main criticisms of the EMMA approach is that end-member composition is likely to vary seasonally and/or due to changes in flowpaths depending on the antecedent moisture conditions and storm intensity (Hooper *et al.*, 1990; Burns *et al.*, 2001), and this violates the EMMA assumption of temporally invariant end-members. Other common difficulties include identification of suitable end-members, defining their chemical composition, and the correct number of end-members. Defining end-member compositions is a difficult task, however, in smaller catchments with relatively uniform catchment characteristics (e.g. soils, climate and geology) it is a common practice to employ a simple two-component model (Soulsby *et al.*, 2003; Abesser *et al.*, 2006b) based on the hydrochemical response of the streams to storm events. The number of end-members is often selected based on results from a prior analysis such as principal component analysis or factor analysis, mixing diagrams of chemical constituents (Christophersen *et al.*, 1990; Hooper *et al.*, 1990; Hooper, 2001), and hydrometric studies in the catchment (Kendall *et al.*, 1999).

While a two-component mixing model is popular, several studies demonstrate a need for a three-component model to adequately characterise stream flow generation (Hooper, 2001; James and Roulet, 2006). Christophersen *et al.* (1990) and Hooper *et al.* (1990) successfully applied a three-component EMMA to include soilwater, groundwater and hillslope-runoff, while Soulsby and Dunn (2003), in a study in the Allt a'Mharcaidh catchment, have identified three end-members as overland flow, shallow surface flow and groundwater flow sources. Since an EMMA approach does not take into account spatial and temporal variability in end-member composition and catchment characteristics, caution needs to be taken in interpreting the results as the end-members may misrepresent the catchment runoff process (Hooper, 2001). This is because, depending on the distribution of soils and antecedent conditions, different parts of the catchment are important for runoff generation at different times (Billett and Cresser, 1996; Burns *et al.*, 2001; Hooper, 2001)

Although EMMA is a simplification of the complex processes that control dissolved species concentrations (Neal *et al.*, 1997b), the approach can still provide insights into how stream water chemistry varies as a function of processes, such as storm events (Abesser *et al.*, 2006a). The main advantage of EMMA over the other methods of hydrograph separation techniques is that it allows the use of direct field measurements in the modelling, thereby facilitating direct linkage of catchment processes to model elements (Burns *et al.*, 2001; Hooper, 2001). Many studies have applied EMMA successfully for hydrograph separation using time series of stream water chemistry, and direct measurements and/or inferred levels of end-member chemistries (Soulsby *et al.*, 2003; Abesser *et al.*, 2006b; Gkritzalis-Papadopoulos *et al.*, 2011).

In this study, an EMMA approach is adopted because it can provide a basis for estimating the contribution of different hydrological sources, and help to improve understanding of the pathways and export mechanisms for chemical constituents, such as DOC and metals. The following sections detail the technique, assumptions, selection of end-members and a summary of the results.

6.4.1. EMMA approach

Several studies have used hydrograph separation techniques such as EMMA to identify the principal sources of stream flow generation (Buttle, 1994; Burns *et al.*, 2001; Soulsby *et al.*, 2003; James and Roulet, 2006). EMMA is a linear mixing approach that uses tracers to identify sources assuming conservative mixing. This technique generally employs isotopes (Buttle, 1994; Brown *et al.*, 1999a; Burns *et al.*, 2001) and chemical tracers (Soulsby *et al.*, 2003; Abesser *et al.*, 2006b; Neill *et al.*, 2011) to solve a mass balance equation in order to determine the proportion of water inputs to stream from each end-member or source. In this study, a chemical tracer method is adopted to investigate the hydrological pathways. Calcium (Ca) and magnesium (Mg) are chosen as tracers based on the following observations: a) they have a relatively strong correlation with flow, b) they are relatively abundant in all subsurface solutions and dominate during low flows (Chapman *et al.*, 1997); and c) there are differences in concentrations between the end-members, as emphasized by Hooper *et al.* (1990). Moreover, these cations are largely replaced by metal ions, such as Mn and Al, which constitute the principal exchanged elements, hence, they are good tracers to distinguish groundwater from soil water and rainwater (Joerin *et al.*, 2002).

A two to n-component mixing model (Pinder and Jones, 1969; Robson and Neal, 1990) is used to separate the streamflow components. This approach has been successfully applied to conservative tracers such as alkalinity (Abesser *et al.*, 2006a) and Ca (Gkritzalis-Papadopoulos *et al.*, 2011) where the following mass balance equations were used to define a two-component flow:

$$Q_{streamwater} = Q_{groundwater} + Q_{soilwater}$$

(Eq. 6.1)

$$Q_{streamwater} \times Ca_{streamwater} = Q_{groundwater} \times Ca_{\ groundwater} + Q_{soilwater} \times Ca_{soilwater}$$

(Eq. 6.2)

where, Q is discharge ($m^3.s^{-1}$), Ca is calcium concentration and the subscripts streamwater, groundwater and soilwater refer to those sources; the latter two are the identified end-members. From the two above equations *(Eqs. 6.1 & 6.2),* the proportion of groundwater can be defined by:

$$\%_{\ groundwater} = 100 \times \left(\frac{Ca_{streamwater} - Ca_{soilwater}}{Ca_{groundwater} - Ca_{soilwater}}\right)$$

(Eq. 6.3)

Application of this approach is based on the following assumptions:

1) As a first approximation, it is assumed that the total stream flow at any given time is a mixture of two flow components with distinct chemical signatures (Christophersen *et al.*, 1990).
2) These components are a groundwater end-member that contributes during lowflows or 'baseflow' conditions, and a soilwater end-member contributing during peak or storm flow.

3) Stream water chemistry is controlled by physical mixing rather than by equilibrium chemistry (Hooper, 2003), thus uniquely identifying the proportions of the two end-members at any given time.

4) End-members within each sub-catchment, to a first approximation, are spatially and temporally invariant (Christophersen *et al.*, 1990; Wade *et al.*, 1999).

These assumptions simplify the existing complex hydrological processes in the River Dyke catchment, in order to allow some general understanding of hydrological setting in the catchment. However, a simple two-component model is deemed appropriate, as this number of factors explain the majority of the variance in the chemistry data (*Section 6.2)*, and it is considered adequate for the purpose of this study which attempts to provide a simple representation of the changing contribution of soil water and groundwater sources. This is in agreement with similar studies carried out in other upland catchments (Billett and Cresser, 1992; Giusti and Neal, 1993; Wade *et al.*, 1999; Soulsby *et al.*, 2002), which have demonstrated that the majority of variability in stream water was explained by changes in groundwater and soilwater contributions.

In this study, soilwater is classified as 'shallow' soilwater that comes from depths between 0 and 50 cm (acrotelm layer) of soil profile and 'deep' soil water, which comes from depths > 50cm (catotelm layer) and extends down to the surface of mineral/bedrock weathering zone (see *Figure 3.3*). Groundwater is essentially considered as the water coming from mineral zones that contain signatures of weathering derived base cations (for example, Ca and Mg).

During base flow conditions, stream chemistry reflects the effects of bedrock weathering, and thus stream chemistry is marked by the signature of

deeper (B/C) soil horizons or groundwater sources. Equally, during peak or high flows, stream water chemistry is dominated by the constituents from surface and shallow-surface (O/A) soil horizons. However, studies have demonstrated that even at high flows, groundwater can contribute significant amounts to streamflow (Soulsby *et al.*, 1998; Burns *et al.*, 2001; Abesser *et al.*, 2006b). Hence, even at peak discharges, streamflow is still a mixture of groundwater and soilwater. The proportion of water from these two end-members varies during and after the storm events, which can be estimated by using EMMA.

Hooper *et al.* (1990) used end member mixing analysis to demonstrate that different flow paths dominate under different antecedent moisture conditions; depending on the discharge history, the signature of end-members may either come from a riparian zone (and/or near stream areas), or from more distant but hydrologically connected parts of the catchment. However, the proportions of different soils immediately adjacent to the streams have much greater impact on the stream water chemistry than those soils at further distances in the catchment (Billett and Cresser, 1992).

Stream chemistry provides information on hydrological pathways when chemically inert solutes that are delivered conservatively through the catchment are used for the hydrograph split (Peters and Ratcliffe, 1998). Calcium is used as a conservative tracer for hydrograph separation (Wade *et al.*, 1999; Joerin *et al.*, 2002; Gkritzalis-Papadopoulos *et al.*, 2011) and its conservative behaviour can be inferred from the matrix plots *(Figure 6.1 - Figure 6.3)*, and confirmed through its simple linear relationship with Mg (another conservative tracer used in this study). These two tracers are characteristic of groundwater (Chapman *et al.*, 1999) and when they are used for hydrograph

separation, the results explain the geographic source (or hydrological flowpaths) by delineating soilwater and groundwater and their contribution, rather than the residence time of water. This allows us to estimate the proportions of two source components so that runoff responses of individual sub-catchments can be compared.

6.4.2. End-members

In this study, it was assumed that the streamwater samples taken under low flow conditions, derived from flow duration curves *(*shown in *Figure 6.8)*, are representative of groundwater end-member (Wade *et al.*, 1999; Soulsby *et al.*, 2003; Abesser *et al.*, 2006b). Therefore, the groundwater end-member ($C_{groundwater}$) was defined as the average tracer concentrations (Ca, Mg) of the lowest flows recorded at each monitoring site. In all the sites, lowest flows, occurred during 26 - 30 August 2010, were used to estimate the groundwater end-member. High flow samples are chosen based on the Q_5 values *(*see *Figure 6.8)*.

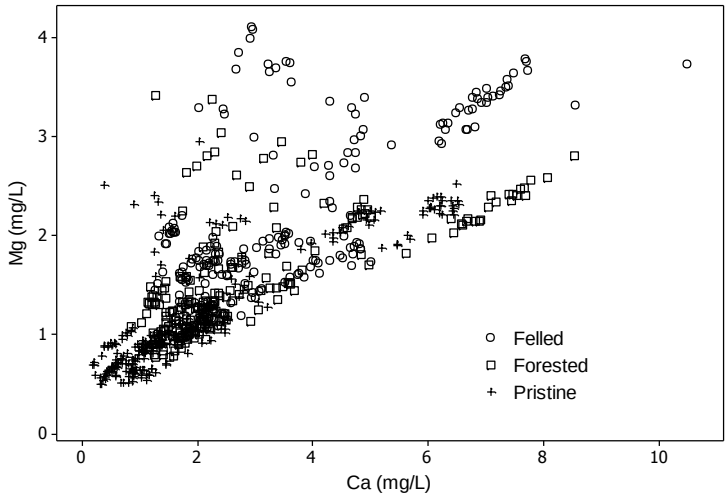


Figure 6.9: Scatterplots showing relationship between Calcium (Ca) and Magnesium (Mg).

Soil water samples taken from a depth of 30-50 cm in each monitoring site are used to define soilwater chemistry. In this case, it has been assumed that the

spatial and temporal variation in the tracer concentrations in soil waters is not significant given the low Ca, Mg concentrations from these sources in the sub-catchments. Thus, the soilwater end-member ($Ca_{soilwater}$) was defined as the average tracer concentrations (Ca, Mg) measured from the above depths. The end-member concentrations for each site are listed in *Table 6.2.*

For the Ca and Mg end-member values listed in *Table 6.2*, mixing plots for each site show that a larger proportion of the stream water samples fall within the triangle enclosed by groundwater, soilwater and high flow (mixture of other two end-members) end-members for both the intact and forested sites, however some samples fall outside the triangle *(Figure 6.10)*. In contrast, most of the streamwater samples fall outside the triangle formed by the end-members in the felled site. These samples could possibly suggest non-conservative mixing or that the controlling end-members have varying compositions through time (Christophersen *et al.*, 1990), and this is evident from the values for Mg which are not much different between two end-members *(Table 6.2)*.

When rainwater/throughfall composition reported for similar catchments (Cresser and Edwards, 1987; Soulsby *et al.*, 1999) is plotted onto *Figure 6.10*, they plot close to the highflow point (HF) in each plot. However, there seems to be some uncertainty in the definition of soilwater end-member inherited from the uncertainty in the tracers (especially Mg). Based on the findings from the factor analysis, a two-component model (Pinder and Jones, 1969; Robson and Neal, 1990; Abesser *et al.*, 2006b) was deemed appropriate for this study, as this approach can still provide insights into variability in streamwater chemistry during storm events in order to learn more about the processes and pathways of carbon export.

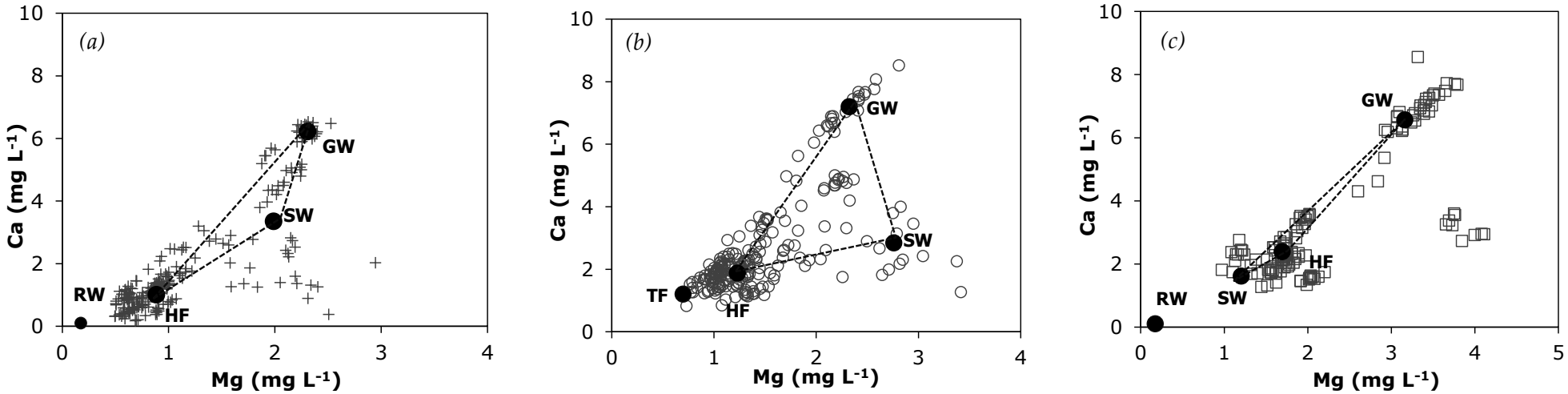


Figure 6.10: Mixing diagrams of calcium and magnesium for the a) intact, b) forested, and c) felled sites, with mean end-member concentrations (solid circles). GW - groundwater; SW - soilwater; HF- High flow; RW – rainwater; and TF – throughfall values taken from Cresser and Edwards (1987) and Soulsby et al. (1999).

Table 6.2: End-member tracer concentrations (mgL^{-1}) for the sites

	Groundwater end-member		*Soilwater end-member*	
Site	Ca	Mg	Ca	Mg
Intact Site	6.2	2.3	3.3	2.0
Forested Site	7.2	2.3	2.8	2.8
Felled Site	6.6	3.2	1.6	1.2

6.4.3. Hydrograph Separation using EMMA

The soil water and ground water end-member concentrations from *Table 6.2* are substituted into *Eq 6.3* to estimate groundwater proportion for any given point of time for which streamwater Ca data are available. Here, groundwater proportions are calculated from streamwater chemistry, rather than from stream discharge values, therefore lags in catchment response (hysteresis) can be evaluated (Foster *et al.*, 2001; Abesser *et al.*, 2006b).

The plots *(Figure 6.11 - Figure 6.13)* clearly highlight the variations in soilwater and groundwater contributions to streamflow during different events, and between sites. Groundwater contributions at all sites are as much as 100% during low flow periods (*e.g.* 27 July 2010 - 30 July 2010) when sub-catchments witnessed long dry antecedent conditions. Despite the differences in proportions of groundwater and soilwater between the sites, a similar pattern of nearly equal proportions of soilwater and groundwater are evident in all sites during the earlier and later stages of events *(Figure 6.11 - Figure 6.13).* A rapid increase in soilwater influence during stormflow is seen in all three sites.

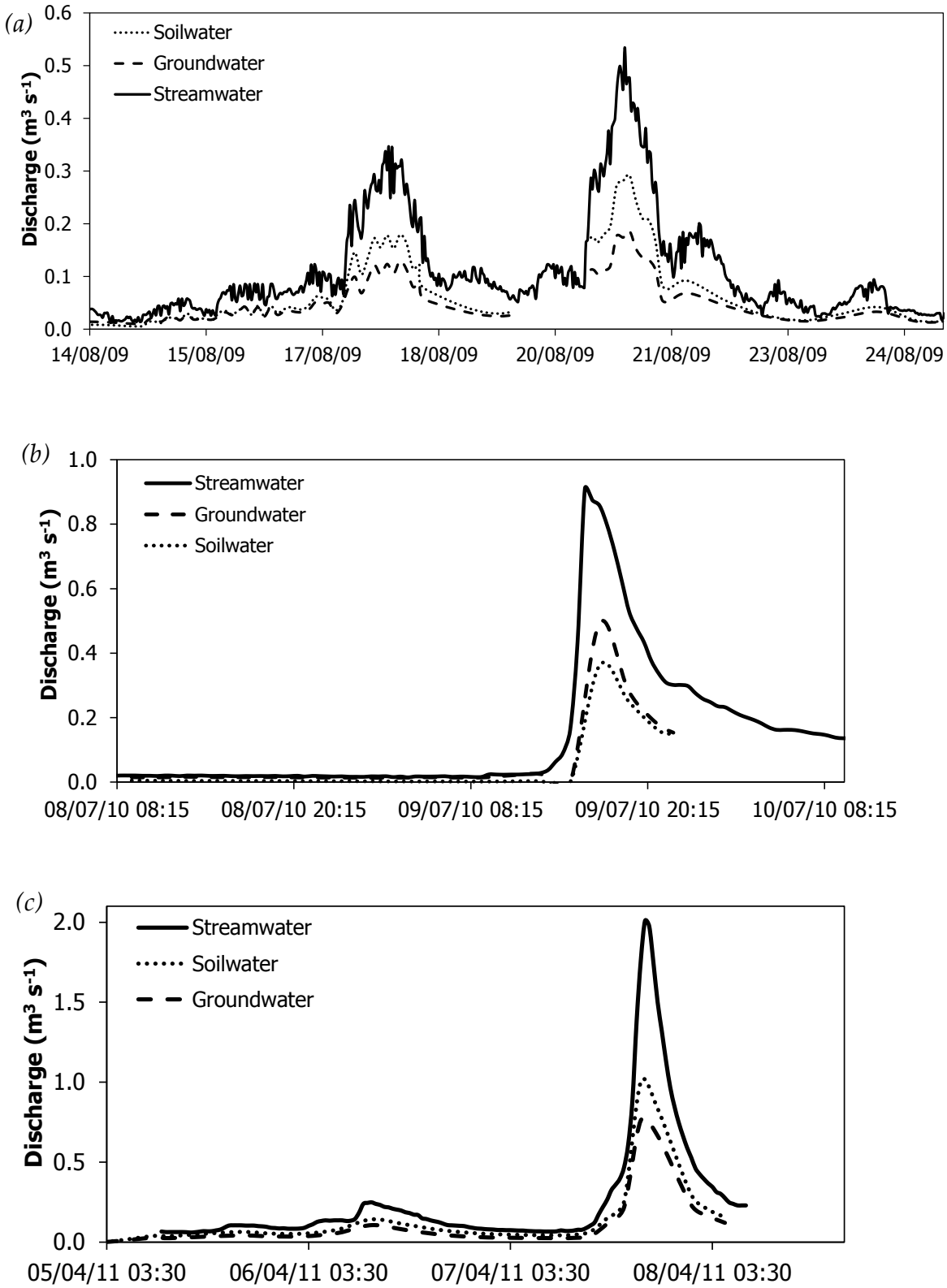


Figure 6.11: Hydrograph separation for the intact site during the events: a) August 2009, (b) July 2010, and (c) April 2011.

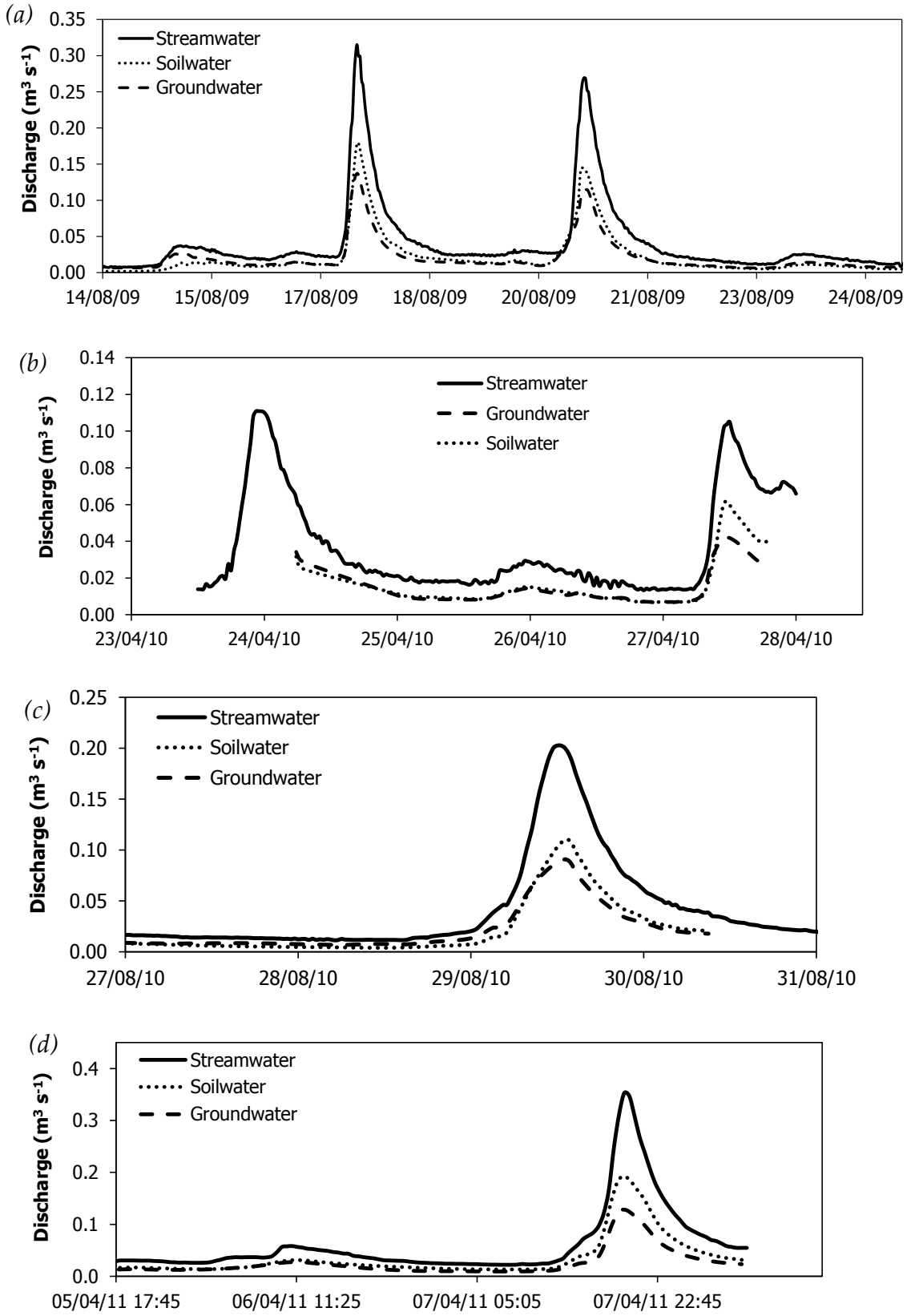


Figure 6.12: Hydrograph separation for the forested site during the events: a) August 2009, (b) April 2010, (c) August 2010, and (d) April 2011.

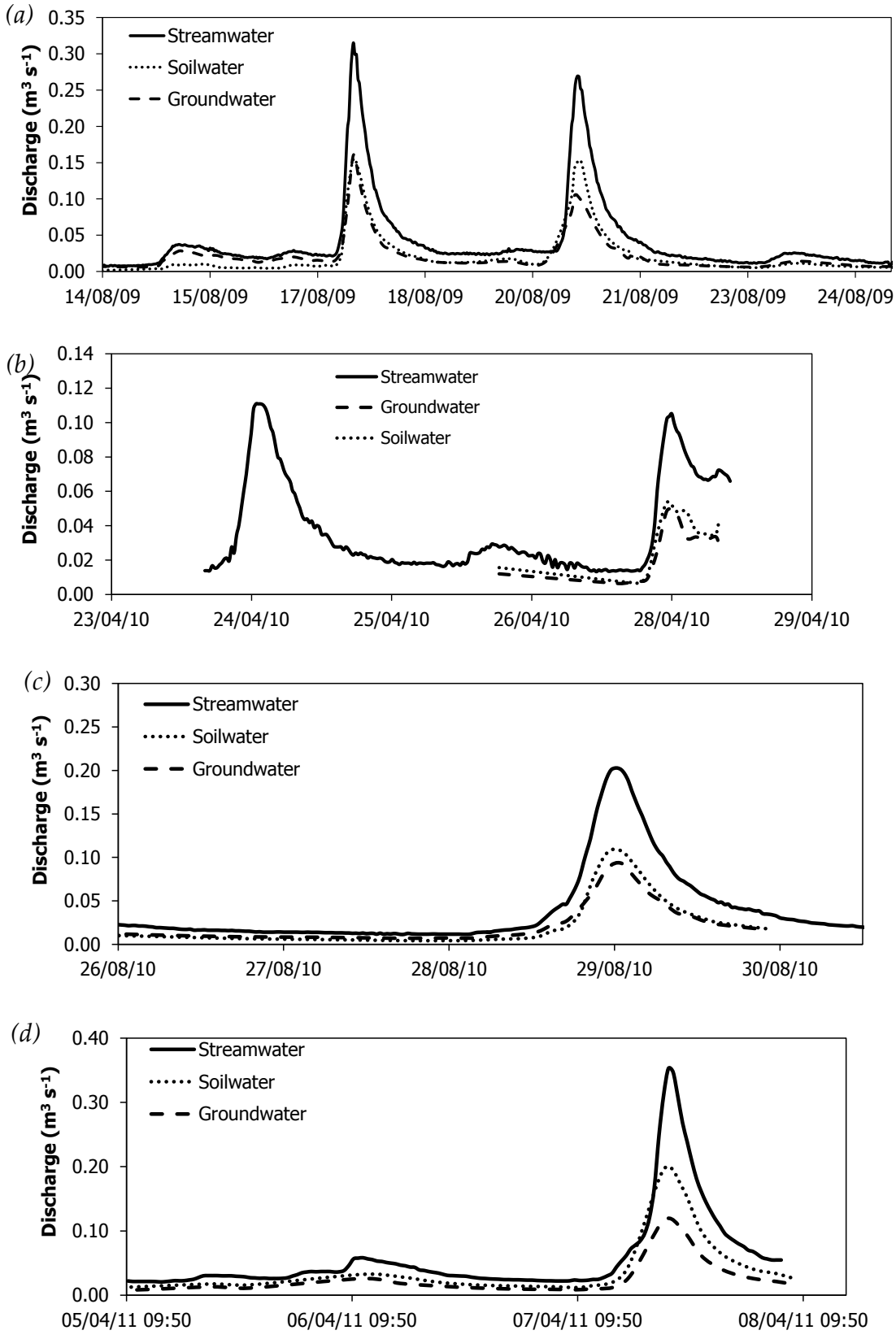


Figure 6.13: Hydrograph separation for the felled site during the events: a) August 2009, (b) April 2010, (c) August 2010, and (d) April 2011.

During storms that follow prolonged dry periods, it takes < 2 hours, ~ 4 - 6 hours and ~ 8 hours (after the onset of an event) for the soilwater proportion to exceed groundwater fraction in the intact, forested and felled sites, respectively , during storm events that follow wet antecedent conditions, soilwater fraction dominates throughout an event *(Figure 6.11 - Figure 6.13)*. Therefore, during an event following dry antecedent conditions, groundwater appears to be a significant source until the soil saturates before contributing to the stream flow. Although, the hydrophobic nature of peat may lead to overland flow (Goulsbra and Evans, 2011), roughness due to landcover *(e.g. Sphagnum or tree cover)* may encourage infiltration (Holden *et al*., 2008).

Minimum, maximum and mean values of soilwater and groundwater fractions and the uncertainties in the estimates are listed in *Table 3* of *Appendix IV*. Average groundwater fractions estimated from measured Ca concentrations for the sampling period (2009-2011) are about 55.3 (±1.2) % at the intact site, 56 (±1.2) % at the forested site, while it is ~ 62 (±1.5) % at the felled site. Similarly, mean soilwater proportions for the same period are, 44.7 (±1.23) %, 44 (±1.19) %, and 38 (±1.5) % in the intact, forested and felled sites, respectively.

The contribution of groundwater and soil water over the entire sampling period can be estimated using the time-series of stream flow, and the robust relationship between instantaneous flow and the proportion of groundwater *(Figure 6.14)* without requiring continuous Ca data, as used in similar studies (Foster *et al*., 2001; Jarvie *et al*., 2001; Abesser *et al*., 2006b). Regression equations and coefficient of determination (R^2) values for individual sites and all sites combined are listed in *Table 6.3* for comparison. From the table, it is evident that the significance of the correlations is not very strong and explains only about 30% – 45% of the variance.

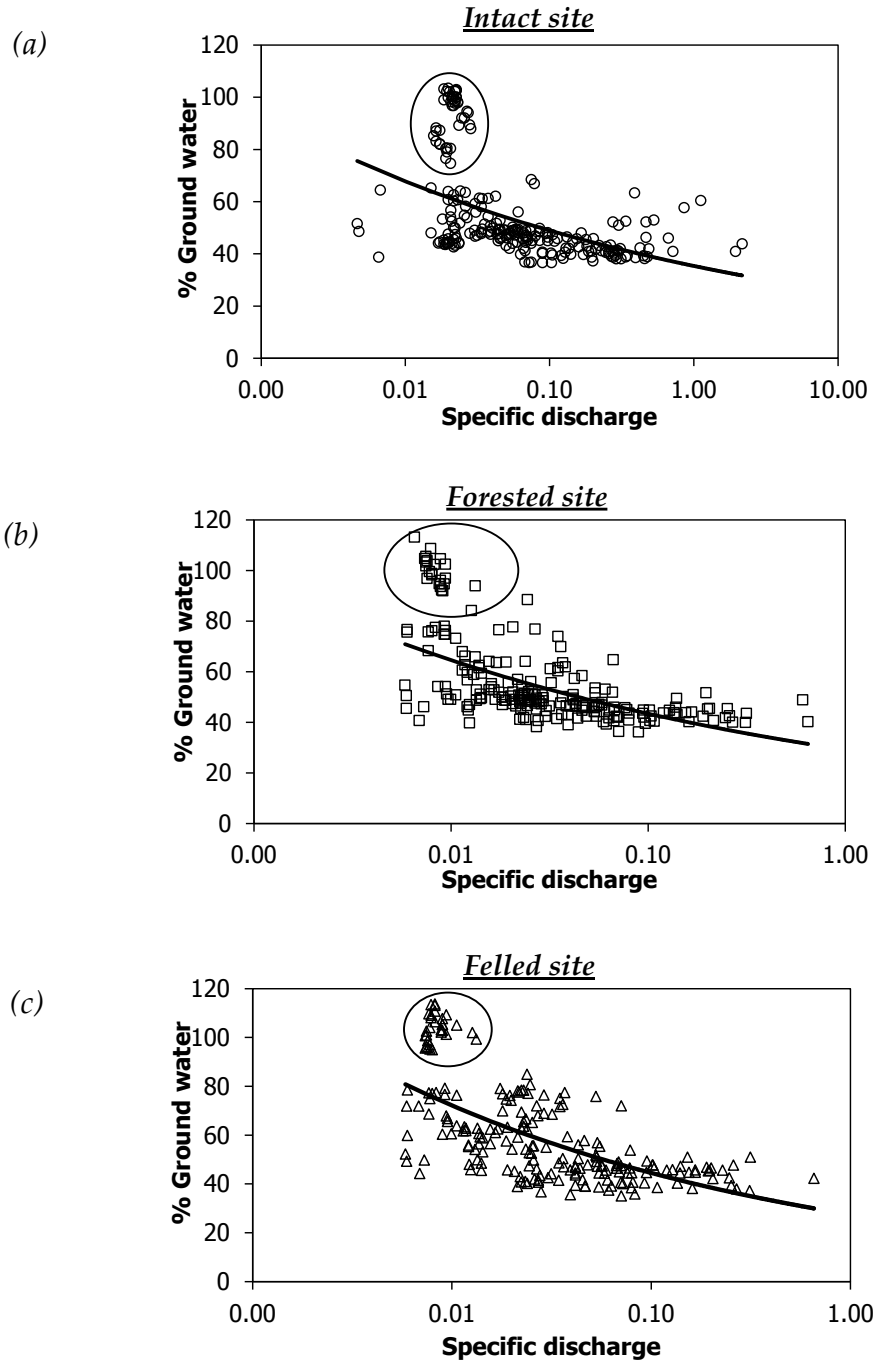


Figure 6.14: Relationship between groundwater proportion and streamflow at the, a) intact, (b) forested, and (c) felled sites. Samples encircled are from low flow dry period in August 2010. Specific discharge in $m^3 s^{-1} km^{-2}$.

The main disadvantage of fitting a single regression line to the data is that it discounts the effects of hysteresis and antecedent conditions, which are especially evident at low flows *(Figure 6.14)*. Thus, this method is a first

approximation and the uncertainties associated with such an approach are acknowledged and quantified (see *Table 3* of *Appendix IV*). Yet, this method is a useful tool for approximating the relative proportions of groundwater and soilwater contribution (Abesser *et al.*, 2006a) and provides some insight into the hydrological setting in the catchment.

Table 6.3: Regression equations demonstrating the correlation between stream discharge and groundwater proportion for individual sites and all sites pooled together. Specific discharge in $m^3 s^{-1} km^{-2}$.

Site	Regression Equation	R^2
Intact Site	$\%_{groundwater} = 35.378 \times (specific\ discharge)^{-0.141}$	0.28
Forested Site	$\%_{groundwater} = 29.214 \times (specific\ discharge)^{-0.172}$	0.41
Felled Site	$\%_{groundwater} = 27.633 \times (specific\ discharge)^{-0.21}$	0.44
Pooled	$\%_{groundwater} = 32.547 \times (specific\ discharge)^{-0.158}$	0.36

The fitted equations from *Table 6.3* for individual sites were applied to the time-series of streamflow data. The resulting hydrograph separation and annual variation in groundwater and soilwater proportions for each site over the study period (2010 -2011) are shown in *Figure 6.15*. Generally, groundwater is dominant during summer months (May-August), and soilwater is dominant during the wetter autumn and winter months (September-January), as well as during spring storm events *(Figure 6.15)*. In all the three sites, although soilwater fluctuations occur throughout the year, variability is relatively higher between late spring and summer months where intense storm events following prolonged dry periods commonly occur. Such periods are very important when estimating annual loads of nutrients since storm events that follow prolonged dry periods are generally associated with higher concentrations of

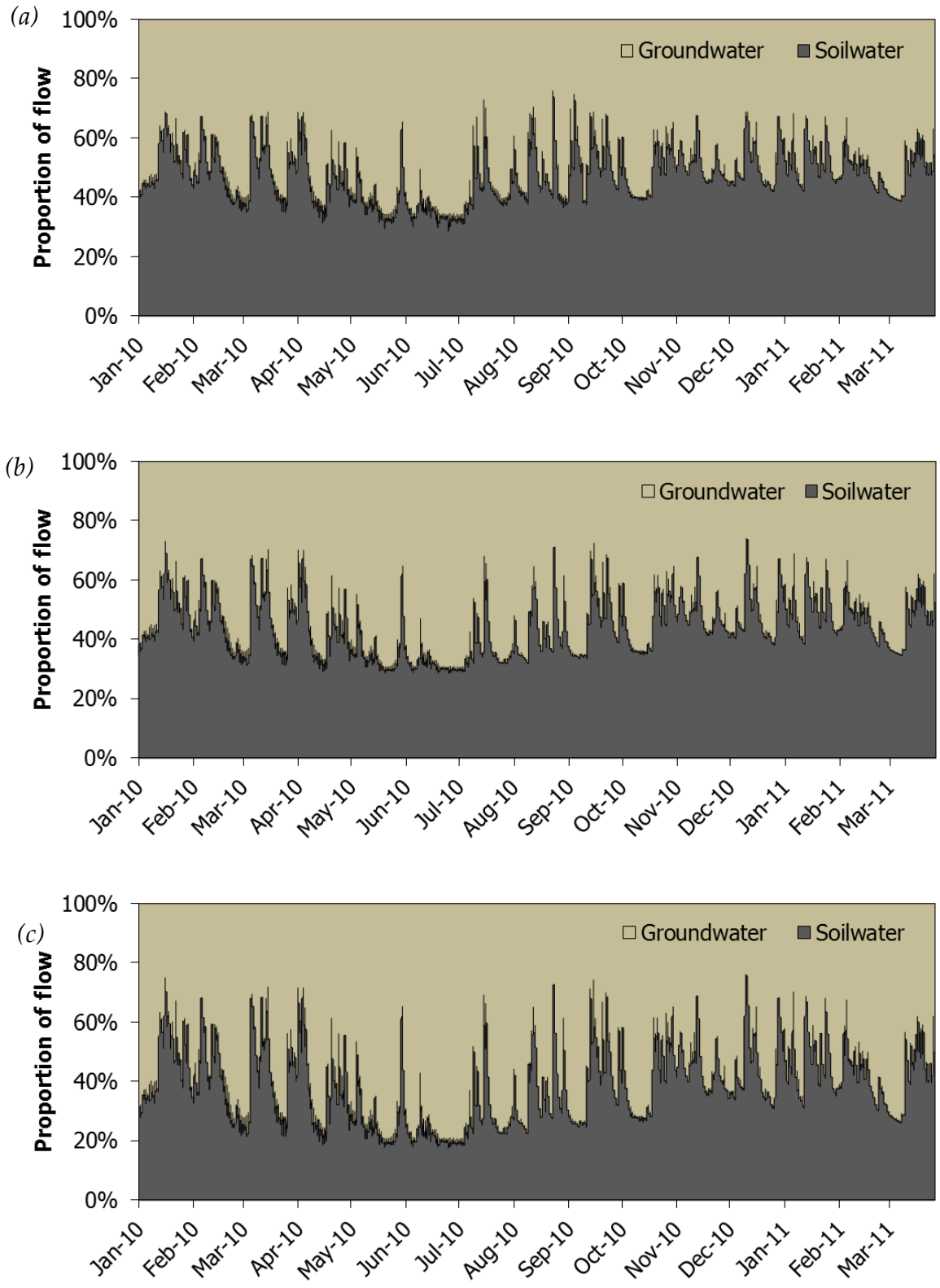


Figure 6.15: Groundwater and soilwater proportions reconstructed using streamflow time series data: a) intact site, (b) forested site, and (c) felled site

nutrients, organic carbon and metals in solution (Freeman *et al.*, 2001; Inamdar *et al.*, 2006; Clark *et al.*, 2007; Worrall *et al.*, 2008).

From the graphs, it can be inferred that in the River Dyke catchment, higher concentrations of dissolved organic carbon and metals are exported in summer months, which is consistent with the higher concentrations of these chemical parameters measured for the same period (see Chapter 5). Differences in the variability of groundwater and soilwater fractions between the sites are evident from the graphs *(Figure 6.15)*, which probably reflect the differences in preferential flowpaths. For example, in the felled site, groundwater proportion is relatively high throughout the year compared to the other two sites. This reflects that infiltration during storm events could be a dominant process, arising due to reduced surface runoff because of felled tree litter and blocked drains (Wilkie and Mayhew, 2003). This flow path may continue to limit soilwater fraction until the peat profile is sufficiently saturated to generate soilwater contribution in the form of subsurface and overland flow (Brown *et al.*, 1999b; Evans *et al.*, 1999; Holden and Burt, 2003).

In order to test the applicability of the derived EMMA model to reconstruct the streamflow components from streamwater chemistry, the correlations between groundwater proportion and stream Mg concentrations for individual sites *(Figure 6.16)* and the resultant regression equations have been used. Mg concentrations are predicted for all samples and compared with the measured values using the EMMA model produced above.

The linear regression relationships between predicted and measured Mg concentrations for each site are shown in *Figure 6.17*; slopes and coefficients of determination (R^2) of regression, all significant at $p < 0.001$, are listed in *Table 6.4*. The results show that Mg concentrations predicted using EMMA model

seem to be overestimated by 0.36 mg L^{-1} (30%), 0.84 mg L^{-1} (55%) and 1.16 mg L^{-1} (54.7%) for the intact, forested and felled sites respectively. Lower slope values for these sites suggest overestimation of Mg during low flows and underestimation at high flows, yet general trends are well captured although R^2 values are not very high.

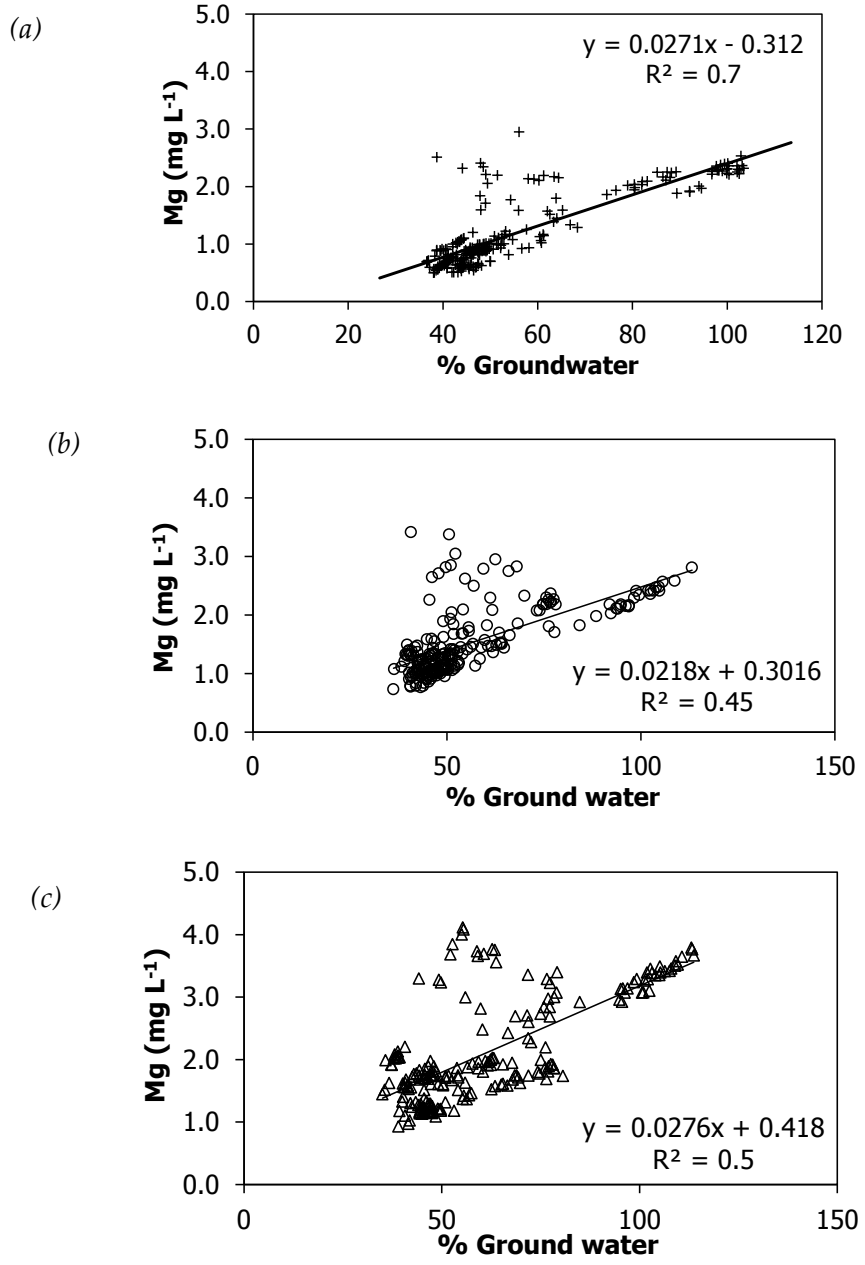


Figure 6.16: Relationship between Mg concentrations and groundwater proportion at (a) intact (b) forested, and (c) felled sites. All significant at $p < 0.001$.

On a closer look at the trend lines *(Figure 6.17)*, it is apparent that the derived EMMA model explains the variation considerably well at high- and low-flows but the spread of points (uncertainty) at high flows could be due to the hysteresis and non-conservative behaviour of Mg (Chapman *et al.*, 1997), as evident from *Figure 6.16.*

Table 6.4: Regression equations and coefficients of determination of regression (R^2) demonstrating the correlation between predicted and measured Mg concentrations for individual sites. All significant at $p < 0.001$.

Site	Regression	R^2
Intact Site	$Mg_p = 0.70 \times Mg_m + 0.36$	0.70
Forested Site	$Mg_p = 0.45 \times Mg_m + 0.84$	0.44
Felled Site	$Mg_p = 0.44 \times Mg_m + 1.16$	0.38

p - predicted; m - measured

DOC and metal concentrations are plotted against proportion of soilwater to see how best the EMMA model fits the data. R^2 values for each element for individual sites are listed in *Table 6.5*. From the table, it is evident that soilwater component in the EMMA model explains the variability in Fe and Mn concentrations for individual sites. Fe correlates inversely with soilwater proportions and the correlations are strong in the intact and felled sites, however they are weak in the forested site. Mn correlates positively in the intact and forested sites and inversely in felled site; however, these relationships are weak. When these correlations are compared with the relationships of the sites with groundwater proportions, it is apparent that Fe and Mn (and also Al in the forested site) exhibit non-conservative behaviour, and suggest near-stream deeper soil sources where reductive solution of Fe and Mn oxides and hydroxides is possible under low redox conditions (Abesser *et al.*, 2006a).

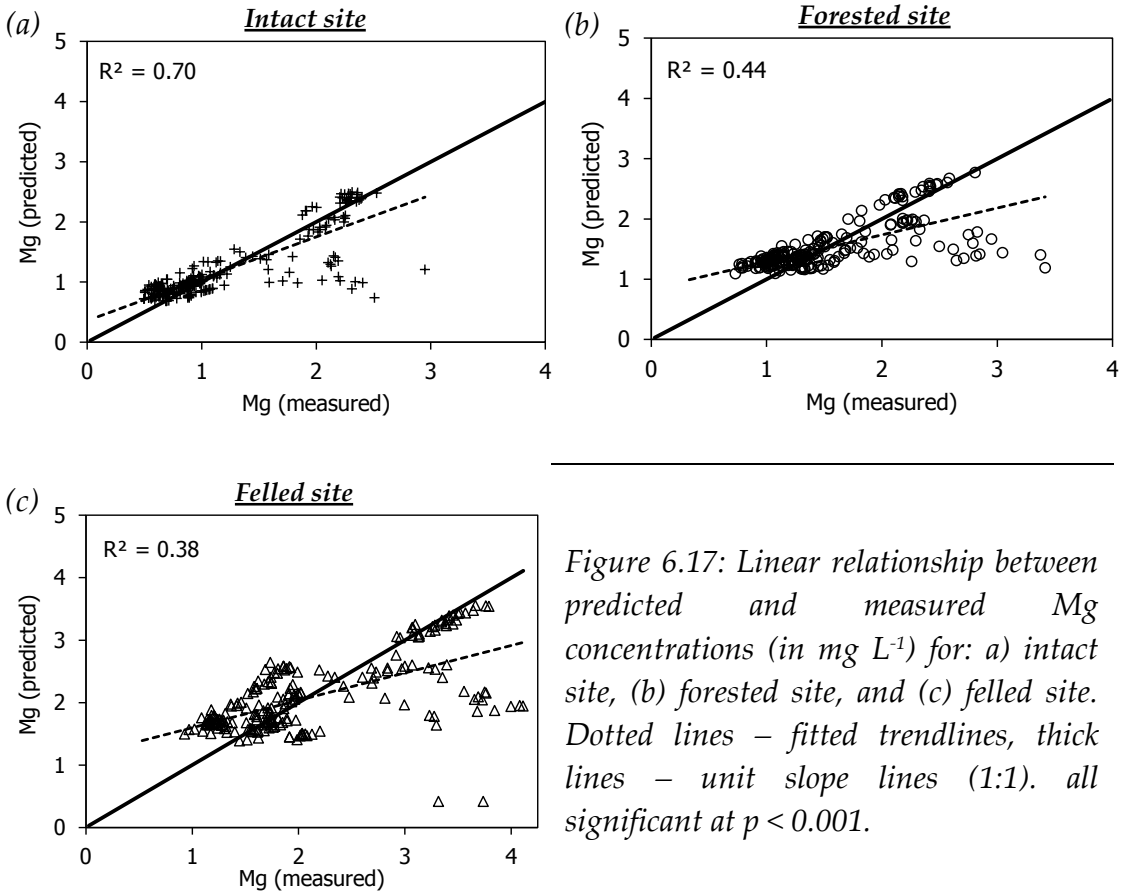


Figure 6.17: Linear relationship between predicted and measured Mg concentrations (in mg L^{-1}) for: a) intact site, (b) forested site, and (c) felled site. Dotted lines – fitted trendlines, thick lines – unit slope lines (1:1). all significant at $p < 0.001$.

Table 6.5: Coefficients of determination (R^2) of linear regression between DOC and metal concentrations, and soilwater proportions for the sites.

Site	Fe	Mn	DOC	Al	Ti
Intact Site	*0.42a	0.27 a	0.01	0.00	0.03
Forested Site	*0.14 a	0.26 a	0.08	0.26 a	0.06
Felled Site	*0.48 a	*0.37 a	*0.03	*0.00	*0.03

* Negative correlation; a at $p < 0.001$

In the intact and forested sites, DOC, Al, and Ti correlations (listed in *Table 6.5*) with percent soilwater are very weakly positive, except for Al in the forested site (0.26), while the correlations in the felled site are weakly negative. This indicates that DOC, Al and Ti are sourced from a same region of peat in

each sub-catchment. In order to explain such weak correlations, the data were inspected, and it was found that correlations of all the above elements with soilwater proportion are strong during the first 40% of soilwater contribution, but once the proportion rises beyond 40% the relationships become complex and tend to weaken. Not surprisingly, the reason for this could be the hysteresis in the dissolved species as the proportions are derived from streamwater chemistry. A third component such as surface flow or shallow subsurface water component from the top 30cm of the peat profile (for which data are not currently available) may explain the unaccounted variability in DOC and Al/Ti concentrations, as the soilwater end-member chemistry presented here represents 30 - 50 cm depth of peat profile.

6.5. Discussion

Streamwater chemistry has been used to investigate the underlying structure between the chemical variables and the streamwater samples from individual sites. Factor analysis (R-mode and Q-mode) and End-member mixing modelling techniques were used to get an insight into the behaviour of each sub-catchment in the River Dyke catchment and to understand the hydrological setting in the catchment, particularly during storm events. Thus, this study attempted to: a) identify the major hydrological pathways during storm events, b) spatial and temporal variability in flow pathways due to differences in landuse, and c) investigate the mechanisms responsible for the export of DOC and associated metals.

The results of factor analysis clearly demonstrated that (during storm events) soilwater inputs coupled with changes in flow pathways are a major control on streamwater chemistry, and emphasize the impacts of changing flow paths on streamwater composition. This has been later confirmed by end-

member mixing analysis (EMMA). The results from EMMA show that soilwater has a greater influence on the stream chemistry with the proportions rising up to 65% during high flows diluting the groundwater signal. However, groundwater inputs also show an increase, during high discharges, reaching to as much as 40-50% of the total stream discharge. Such a buffering of stream chemistry by groundwater inputs at high flows has been reported in other similar studies (Soulsby *et al.*, 2005; Abesser *et al.*, 2006b).

Factor analysis results helped in identifying the two important sources of streamflow generation in the form of extracted factors. Thus, a soilwater component and a groundwater component were identified, as no other significant component was evident from the results. Subsequently to investigate hydrological pathways and sources of streamflow generation during storm events, end-member mixing analysis was undertaken. The factors extracted in factor analysis were used to define end-members in EMMA, similar to approaches adopted in other studies (Reid *et al.*, 1981; Soulsby *et al.*, 2003; Abesser *et al.*, 2006b). The nature of the end-member compositions and the number of end-members are generally assumed (Uhlenbrook and Hoeg, 2003), however, this study uses the factor analysis findings as a basis for the EMMA. Moreover, in this study factor analysis was performed using a principal component analysis approach, which does not *a priori* assume the number or nature of end-members.

The results from the hydrograph separation identified the flowpaths of water that are crucial in understanding the catchment processes such as overland flow, subsurface runoff, erosion as these processes mobilize nutrients, organic carbon and associated metal ions, and also satisfactorily explained the temporal and spatial variability in stream water chemistry, which are in

agreement with the findings of factor analysis. In all the sub-catchments, the groundwater end-member is characterised by high base cation concentrations, while the soilwater end-member is distinguished by high concentrations of DOC, Al, Ti, Mn, and Fe. The changes in Al, Ti are found to be more closely associated with DOC, whilst that of Fe and Mn are not. This suggests that either high Al, Ti concentrations are directly related to increased DOC export (i.e., discharge of water from DOC source regions and that from Al/ Ti sources coincide), or that the DOC and Al/Ti are sourced from the same horizons of peat.

In all the sub-catchments, soilwater and/or groundwater inputs from riparian zones (Smart *et al.*, 2001; Soulsby *et al.*, 2005; Andrews *et al.*, 2011) to stream flow vary at the onset of a storm hydrograph, depending on the antecedent-moisture conditions *(Figure 6.11 - Figure 6.13)*. At the intact site, increasing concentrations of DOC and metal ions at the initial stages of hydrograph suggest that soilwater dominates the flow on the rising limb of the storm hydrograph (see *Appendx V*). However, DOC peaks do not appear to coincide with that of Fe, Mn and Al which may be reflecting a different source for DOC, probably a near-surface source (Brown *et al.*, 1999a; Billett *et al.*, 2006; Clark *et al.*, 2008). Therefore, at this site, the onset of an event is characterized by water from overland and shallow surface sources dominating the soilwater inputs, which surpasses the groundwater inputs from deeper sources within 2 hours of the onset of an event. At peak discharges, soilwater mainly composed of water from relatively deep soil sources dominates the stream flow, giving way to groundwater in the later stages of the hydrograph.

At the forested and felled sites, riparian groundwater seems to dominate the earlier stages of the storm hydrograph gradually giving way to soilwater

during the later stages. This early dominance of groundwater or deep soilwater (soilwater from depths > 50cm extending down to the weathering/groundwater zone) is probably associated with displacement of pre-event water in deeper horizons of the riparian zone as reported by many authors (Giusti and Neal, 1993; Kendall and McDonnell, 1998; Inamdar *et al.*, 2004). This is confirmed by the lags observed in the peak concentrations of base cations, DOC and metal ions relative to hydrograph peaks (*Appendx V*). This inference is in agreement with the factor analysis results, which indicate flushing of pre-event water rich in base cations, Fe and Mn. Such a mechanism highlights the importance of inputs from riparian zone in streamflow generation, especially during the earlier stages of storm hydrograph. However, delay in peak concentrations suggests a possibility of macro-pore flow or the flow through preferential pathways (roots zones, pipes etc.) with relatively less resident times during peak discharges. Water flow through rapid pathways (surface or subsurface) exceed that from deep mineral horizons during dry antecedent conditions, while saturated matrix flow appears to dominate streamflow in wet-antecedent moisture conditions due to expansion of surface saturated areas upslope and steep near-stream hydraulic gradients (Hooper *et al.*, 1990). A similar mechanism was observed by Brown *et al.* (1999a), where they have demonstrated that stream flow during a summer storm is a mixture of three end members: throughfall, O-horizon soilwater, and near-stream groundwater.

In the forested site, a consistent progression of end-member influence on the hydrograph is apparent. For example, a delay in the DOC peak suggests that the stream receives inputs first from rapid flowpaths until the time of peak flow, then from organic-rich soilwater immediately after the hydrograph peak,

and finally from near-stream deep soil or groundwater sources on the receding limb of the hydrograph (Brown *et al.*, 1999a).

At the felled site, although a mechanism similar to that observed in forested site is evident, the soil disturbance due to felling and the additives used on the forestry (before felling) are re-exposed to interact with flowing water, which are reflected in relatively high concentrations of base cations, metals and DOC (Cummins and Farrell, 2003a, 2003b). During peak discharges, although soilwater dominates, a relatively constant supply of base cations indicates the significance of groundwater even during peak flows. Hence, in this site, inputs from groundwater sources are as important as those from soilwater sources.

The EMMA models for individual sites for the entire study period indicate that mean groundwater and soil water contributions are ~55 % and ~45%, respectively, at the intact site, are ~56% and 44% respectively, for the forested site, and are ~62 % and ~38%, respectively, for the felled site. The results suggest that groundwater is the dominant contributor to stream discharge although the relative proportions of groundwater declines during peak discharges. When compared to the felled site, the low mean groundwater proportions observed at the forested site can be explained by evapotranspiration losses from the vegetation, which may reduce groundwater storage (Charman, 2002; Tsutsumi *et al.*, 2004).

Compared to the other sites, groundwater provides most of the runoff in the felled site *(Figure 6.15)*. The dominance of groundwater contribution throughout year in this site is consistent with relatively high base cation concentrations *(Figure 5.6 & Table 5.1)* in the streamwater samples compared to the other sites. It could be that the presence of drain blocks and felled tree litter,

which resist surface and subsurface runoff and delay the release of water, allow percolation to increase groundwater storage. Similarly, at the forested site, the proportion of groundwater or deep soilwater seems to be relatively high compared to the intact site. This could be due to the presence of the tree stand and litter which reduce surface runoff and aid percolation of water to deeper soil sources. This can be confirmed by the range of base cation concentrations reported in this site *(Figure 5.6 & Table 5.1)*.

Thus, the derived EMMA model sufficiently explains the influence of land-use factor in terms of lag in stream chemistry, differences in hydrologic flow paths and differences in proportions of soilwater and groundwater, despite the geology being nearly homogenous. The hydrograph split based on the annual streamflow data can be a very useful tool for future monitoring in the catchment. For example, soilwater proportions related to storm events following long dry periods, for example in summer months, seem to be critical in exporting DOC and associated metals; however, it has a limitation in quantitatively predicting the loads that can be achieved by improving the model further. Hence, this model can be taken into account for planning future sampling programmes. Besides, hydrograph separation based on EMMA produced a simple model that can be used to reproduce contributions of different runoff sources to stream flow during a sampling period.

Although variability in groundwater and soilwater proportions and the associated chemistry are sufficiently explained by the model, another component seems to exist, which is very much a part of soilwater and is responsible for the observed variability in DOC, Al and Ti; the model has provided a hint in identifying that source. This inference is made since the samples that fall outside the sampled source waters *(Figure 6.10)* have generally

been related to unsampled source water or to the evolution of the water (Christophersen *et al.*, 1990; Chapman *et al.*, 1997). For example, during the event on 20 August 2009, the lag between peak discharge and the factor loading peak related to soilwater component *(Figure 6.7)*, and the coinciding decline in the factor loadings related to groundwater component during peak discharges, probably reflect the occurrence of a third end-member, such as overland (Goulsbra and Evans, 2011) or shallow subsurface flow (Brown *et al.*, 1999b).

Overland flow possibly occurs as infiltration excess flow during the events that follow dry conditions due to the hydrophobic nature of peat, and as saturation excess flow during the events with wet antecedent conditions (Goulsbra and Evans, 2011). However, at the intact site, as *Sphagnum* provides effective roughness to minimize overland flow (Holden *et al.*, 2008), shallow subsurface flow could possibly be a third end-member (Worrall *et al.*, 2006b). In the forested catchment, despite the presence of vegetation, significant runoff in the form of overland flow and as shallow subsurface flow through rapid flowpaths (macropores) is possible (Holden *et al.*, 2001, 2004, 2008). At the felled site, although the litter of felled trees and the drain blocks reduce rapid runoff (Holden *et al.*, 2004; Worrall *et al.*, 2007a), surface runoff or near-surface flow is possible above a saturated catotelm, particularly during wet antecedent conditions (Evans *et al.*, 1999). In addition, the component in question may be related to 'near-surface' peat layers as evident from the DOC variability and its relation to Al and Ti, and as reported by several studies (Brown *et al.*, 1999a; Billett *et al.*, 2006; Clark *et al.*, 2008).

Therefore, the uncertainty in the EMMA models for sites could be explained by introducing an additional end-member such as overland or shallow subsurface flow. Despite the uncertainty (18% - 22%) identified related to defining a

shallow soilwater end-member, the EMMA model demonstrated here provides an insight into the hydrological pathways and sources of streamwater in the sub-catchments. Thus, the results of this modelling are a first approximation to understand the hydrological setting in the catchment.

6.6. Conclusions

Sources and flowpaths of streamwater were examined in the River Dyke catchment, at the event scale using hydrometric and natural tracer data. EMMA indicated three main sources for streamflow generation: a) groundwater, b) soilwater and c) near-surface soilwater.

This study has achieved the following goals: i) identified the major hydrological pathways during storm events, ii) explained the spatial and temporal variability in flow pathways due to differences in landuse, iii) investigated the mechanisms responsible for the export of DOC and associated metals.

Nevertheless, the EMMA model can be improved further to overcome the identified limitations, by introducing a shallow surface water component. Therefore, the next step in this study is to investigate for a possible link between near-surface component and its influence on streamwater flow and chemistry, which will be dealt with in the next chapter.

Chapter 7
ORGANIC CARBON

This chapter summarises the spatial and temporal variability in the organic carbon concentrations in the River Dyke catchment; and using the understanding gained from the previous chapters, conceptual models explaining DOC export mechanisms for each sub-catchment are presented.

7.1. Introduction

Peatlands are the principal source of organic carbon to fluvial systems (Hope *et al.*, 1997a). The release of organic carbon (OC) in dissolved (DOC) and particulate forms (POC) to stream runoff is a fundamental part of the fluvial carbon cycle, which has a wide range of influence on fluvial ecosystems, and account for as much as 10% of ecosystem C outputs (Hope *et al.*, 2001; Billett *et al.*, 2004; Limpens *et al.*, 2008). For example, Worrall *et al.* (2009) in a long-term carbon budget study on Trout Beck catchment found that fluvial DOC is the second largest component of the carbon fluxes leaving the catchment (accounting for 26% of C losses) and POC losses accounting for ~9% of residual carbon stored in peats.

Concentrations and fluxes of DOC are sensitive to changes in discharge (Tranvik and Jansson, 2002), temperature (Freeman *et al.*, 2001a), antecedent moisture conditions in the catchment (Turgeon and Courchesne, 2008), landuse management (Worrall *et al.*, 2003a) and hydrological pathways (Worrall *et al.*, 2006a) more detailed description on these controls is provided in *Chapter 2*. Hence, there is a need to establish the controls on the spatial and temporal variability of DOC concentrations. In order to model DOC fluxes under changing climatic conditions, it is essential to identify the underlying

mechanisms, such as changes hydrological pathways related to changes in discharge, that regulate the concentrations/fluxes in a catchment.

Particulate organic carbon forms a significant C export in many peat-dominated catchments and therefore needs to be accounted for when estimating carbon budget for such catchments (Holden, 2005). For example, estimates of POC loss from northern peatlands have been reported to range from 0.12 to 38.8 gC m^{-2} per annum (Labadz *et al.*, 1991; Dawson *et al.*, 2002; Evans and Warburton, 2005) which is as much as DOC loss. In addition, release of POC suggests peat erosion (Holden, 2005), therefore examining the POC concentrations/fluxes from a catchment can provide information about the rate of peat erosion, which can be expressed as sediment yield in any given catchment (Leithold *et al.*, 2006). However, in a study on a Scottish headwater stream Dawson *et al.*, (2001b) found that POC concentrations were very low (0.2-0.8 mg C/L), such studies use the term TOC and DOC interchangeably.

The following chapter focuses on the relationships of DOC and POC with varying discharge and investigates the flow pathways that deliver organic carbon to streams.

7.2. Sampling and data collection

Stream water samples were collected from five sites in the River Dyke catchment: an unmanaged blanket bog (intact site), a forested site, two felled sites and a site close to the outlet of the catchment *(see Figure 5.1)*. Soil pore-water samples were collected from PVC tube wells occasionally from the intact, forested and one of the felled sites from three different depths (30-50 cm, 80-100 cm, and 130-150 cm). Monitoring periods, sampling strategy, sample collection and analysis are outlined in *Chapter 4*. DOC in streamwater and soil pore-water was measured using spectrophotometry and thermal catalytic oxidation (TOC-

analyser) methods, and POC in streamwater samples is measured using loss-on-ignition technique; detailed methodology is provided in *Chapter 4.*

7.3. Spatial and Temporal variability in DOC

Spatial variation in dissolved organic carbon concentrations was evident in samples from different landuse sites *(Table 7.1)*. Of all three sites, DOC concentrations were highest in the felled site, with a maximum reaching up to 80 mg C L^{-1}. In contrast, DOC levels in forested and intact sites are statistically similar to one another, but with the intact site showing slightly higher minimum, maximum and mean DOC values.

Table 7.1: Site-wise descriptive statistics for DOC (mg C L^{-1})

Site	Min	Max	Mean	Std Dev	N
Pooled	2.5	78.8	29.6 ± 0.7	16.8	588
Felled	8.2	78.8	47.2 ± 1.5	18.5	149
Forested	2.5	42.2	20.9 ± 0.7	9.5	188
Intact	4.4	43.9	21.3 ± 0.5	7.7	198

Dissolved organic carbon concentrations show a temporal trend and vary seasonally as evident from *Figure 7.1* and *Table 7.2*. To examine the seasonal variation in the DOC concentrations, data were divided according to seasons defined as winter (December-February), spring (March-May), summer (June-August), and autumn (September-November). A general trend is apparent from the table that in all three sites, DOC concentrations were highest during summer and decreasing through autumn to winter and before increasing again in spring. Between summer and autumn mean DOC values dropped by ~17% in the felled site, 28% in the forested site and 33% in the intact site *(Table 7.2 & Figure 7.1).* A further fall in mean DOC were observed between autumn and winter by ~70% in forested and felled sites and by about 62% in the intact site.

A box plot illustrating the DOC variability across the seasons in all three sites *(Figure 7.1)* reveals that the felled site shows a wide range of DOC values, while in the intact site, the variability is comparatively low, and forested site shows an intermediate range of variability.

Table 7.2: Seasonal descriptive statistics of DOC in mg C L^{-1} for sites.

Season	Site	Min	Max	Mean	Std dev	N
SUMMER	*Pooled*	6.2	78.8	36.4 ± 0.9	16.3	360
	Felled	42.3	78.8	61.1 ± 1.1	9.6	81
	Forested	6.2	42.2	27.1 ± 0.8	8.3	100
	Intact	11.0	43.9	25.8 ± 0.4	5.0	128
AUTUMN	*Pooled*	11.3	73.5	28.2 ± 2.8	16.3	33
	Felled	30.5	73.5	47.9 ± 3.7	12.3	11
	Forested	11.3	28.6	19.4 ± 1.4	4.6	11
	Intact	12.2	30.3	17.2 ± 1.7	5.5	11
WINTER	*Pooled*	2.5	26.4	8.9 ± 1.0	6.1	36
	Felled	8.2	26.4	14.2 ± 2.0	6.8	12
	Forested	2.5	14.2	5.8 ± 1.4	4.8	12
	Intact	4.4	9.4	6.6 ± 0.6	1.9	12
SPRING	*Pooled*	10.3	39.7	18.9 ± 0.6	7.9	158
	Felled	25.3	39.7	30.6 ± 0.5	3.4	46
	Forested	11.1	21.2	14.4 ± 0.2	1.8	65
	Intact	10.3	15.9	13.6 ± 0.2	1.1	47

7.4. DOC and discharge (Q) relationship

Several studies have demonstrated that a significant relationship exists between stream DOC concentrations and discharge (Grieve, 1984; Hope *et al.*, 1997b; Worrall *et al.*, 2002). For example, Clark *et al.* (2008) have found a decrease in DOC with increased stream flow; while in a different study, Worrall *et al.* (2008) have noted an increase as well as decrease in DOC concentrations with stream discharges and concluded that the time between the storm events is the controlling factor for DOC flux/concentrations. However, Bernal *et al.* (2002)

found no correlation between DOC and discharge. Hence, in order to identify the controls on DOC export and to model DOC concentrations, it is essential to establish if a relationship between discharge and DOC concentrations exists.

The regression relationships between DOC concentrations and instantaneous discharge (at the time of sampling), are listed in *Table 7.3*. In order to compare the relationships and fluxes between the sites, specific discharge ($m^3s^{-1}sqkm^{-1}$) is used interchangeably with discharge (m^3s^{-1}).

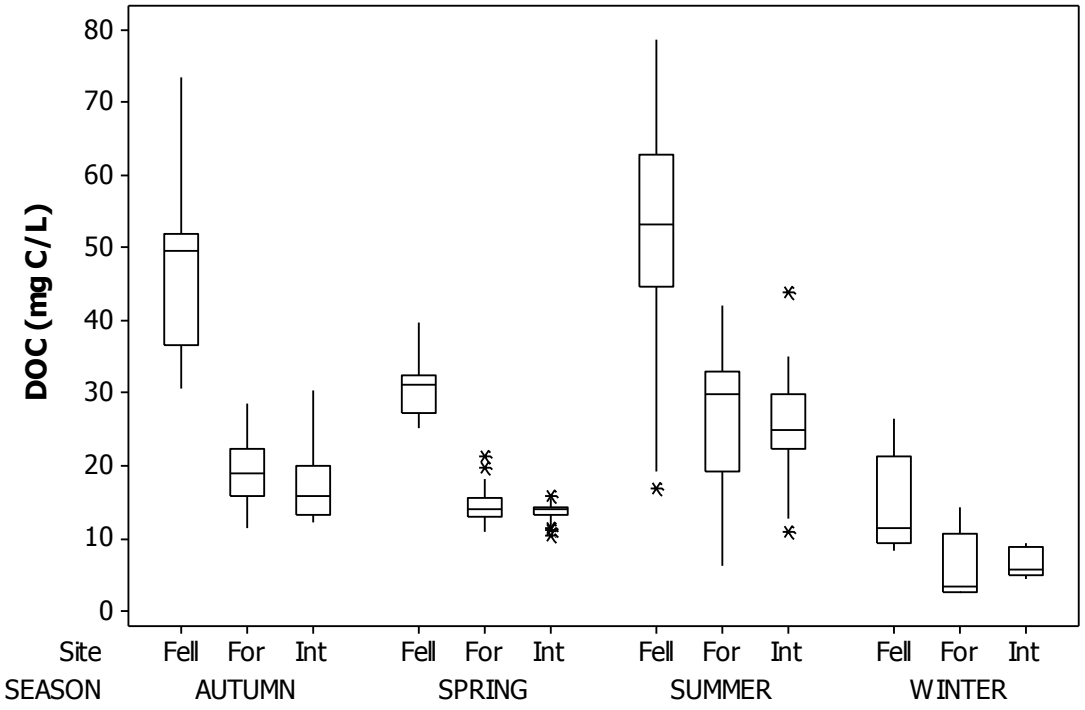


*Figure 7.1: Box plot showing seasonal variability in DOC concentrations in all three sites. Fell - Felled, For - Forested, and Int - Intact sites. Horizontal lines in the box are the median DOC concentrations; outliers are shown as **

Seasonal variations in the DOC – discharge (Q) relationships are apparent from *Figure 7.1* and *Table 7.3*. No relationship was found between DOC and Q when the data from all the cover types was pooled, probably because each land use type showed a distinct DOC - Q pattern. Strong positive relationships between stream flow and DOC are evident during summer, autumn and winter months for the different land use types, while DOC and Q are poorly correlated during spring. Consistently strong DOC-Q relationship is observed for the

forested site with regressions (r^2 values) explaining 63% (summer) and 68% (autumn and winter) variance in the data. Equally, relatively stronger DOC and Q correlations are found in the intact site with the regressions explaining 12% - 55% common variance between the two variables.

Table 7.3: Seasonal variability in the relationship between specific discharge (Q) in $m^3 s^{-1} km^{-2}$) and DOC concentrations in mg C L^{-1} for sites.

Season	Site	Relationship	r^2	N	Std error
SUMMER	*Pooled*	DOC = 0.9 log Q + 39.5	0.004	360	16.3
	Intact	DOC = 3.05 log Q + 34.7	0.55 [a]	128	3.4
	Forested	DOC = 6.23 log Q + 49.2	0.63 [a]	100	5.1
	Felled1	DOC = 6.15 log Q + 62.5	0.54 [a]	52	6.3
	Felled2	DOC = 5.8 log Q + 84.3	0.36 [a]	81	7.7
AUTUMN & WINTER	*Pooled*	DOC = 31.2 $(Q)^{0.337}$	0.22	69	0.8
	Intact	DOC = 19.3 $(Q)^{0.33}$	0.50 [a]	23	0.4
	Forested	DOC = 6.4 log Q + 31.5	0.68 [a]	23	5.0
	Felled	DOC = 14.0 log Q + 72.6	0.53 [a]	23	14.2
SPRING	*Pooled*	DOC = 16.4 $(Q)^{-0.022}$	0.00	158	0.4
	Intact	DOC = 0.43 log Q + 14.7	0.12 [a]	47	1.1
	Forested	DOC = 0.66 log Q + 16.7	0.07 [a]	65	1.8
	Felled	DOC = 35.02 $(Q)^{0.045}$	0.10 [a]	45	0.1

[a] significance at < 0.05

Of the two felled sites, DOC concentrations at felled1 site (sampled only during summer 2009) show a stronger relationship ($r^2 = 0.54$) with discharge and similar correlations is apparent in felled2 site for summer ($r^2 = 0.36$), autumn and winter ($r^2 = 0.53$) periods, however a weak relationship ($r^2 = 0.10$) is found during spring months, all significant at $p < 0.05$.

The logarithmic relationship between DOC concentrations and discharge seems to be dominant in most occasions for all sites except for autumn and winter samples from the intact and pooled data sets, and spring samples from the felled and pooled data sets *(Table 7.3 & Figure 7.5)*.

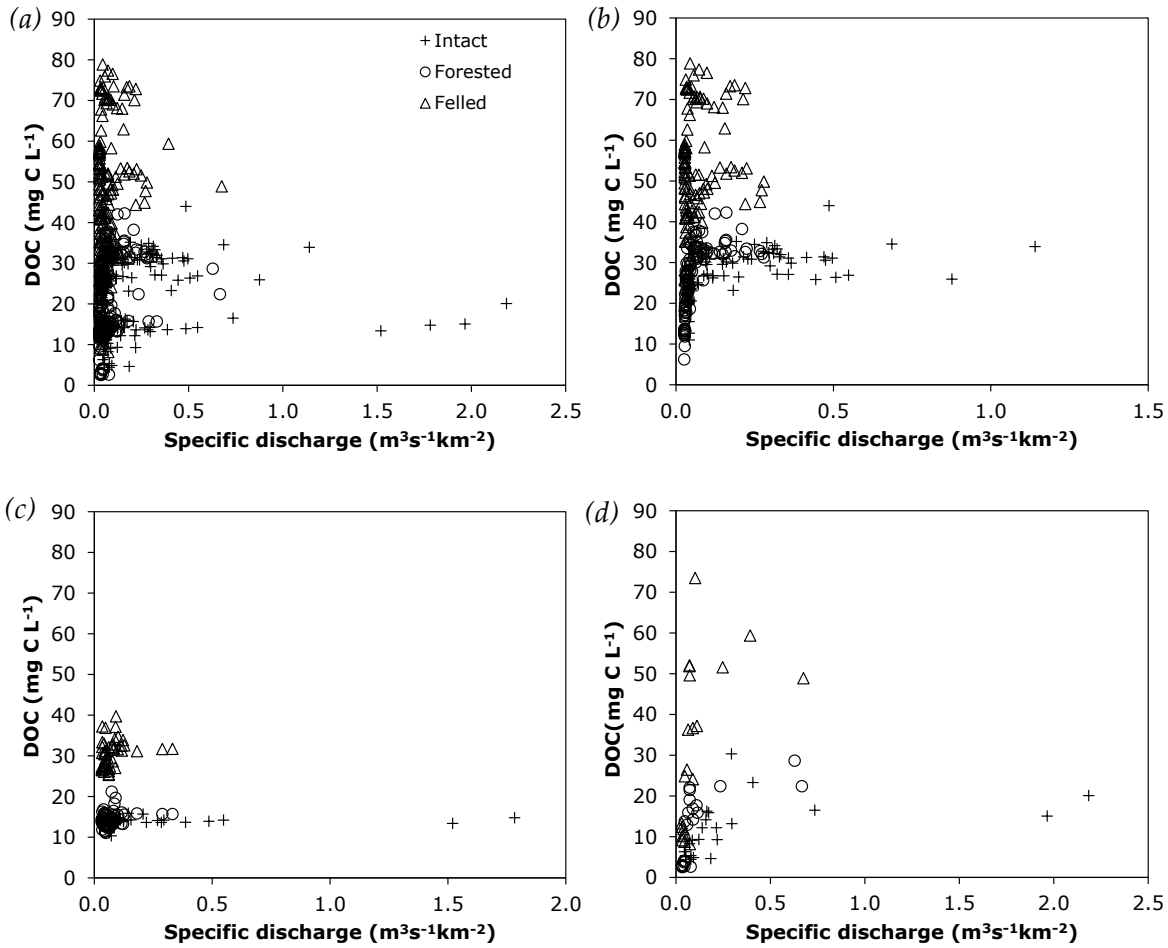


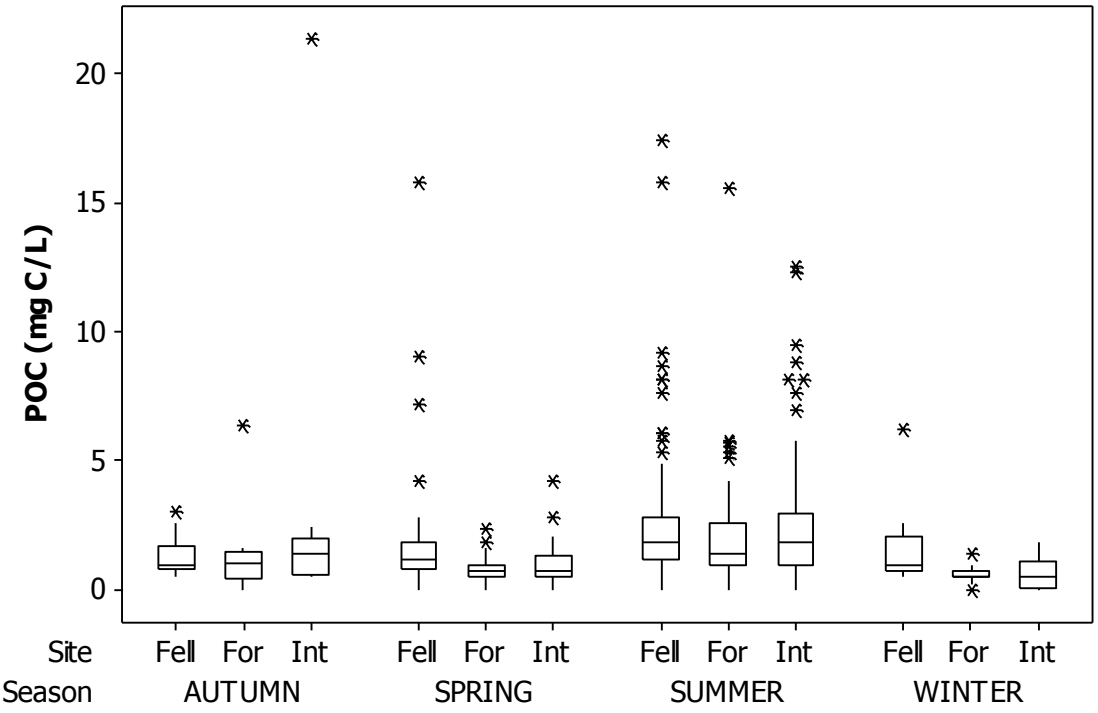
Figure 7.2: Plots showing relationship between DOC concentrations, and specific discharge for all three sites. (a) Pooled data (all seasons), (b) Summer, (c) Spring, and (d) Autumn and Winter.

7.5. Spatial and Temporal variability in Particulate Organic Carbon

POC concentrations in this study vary spatially and temporally as evident from *Figure 7.3* and *Table 7.4*. Minimum POC values are near-zero for the entire study period, while high maximum and mean POC concentrations are associated with summer storm events; except for, a spot sample collected from

intact site during autumn 2009 shows a maximum POC of 21.3 mg C L^{-1}. Mean POC concentrations during summer (~2.3 mg C L^{-1}), are similar for all three sites *(Table 7.4)*. However, autumn mean POC concentrations vary between the sites, decreasing by 44% in the felled site, 26% in the forested site, and increasing by 52% in the intact site compared to that in summer months. During winter, a dip in mean POC of about 57% in the forested site and 83% in the intact site mean POC is evident, a 23% rise in mean POC is seen in the felled site. During the spring period, a further rise of 25% in mean POC was observed in the felled site while an increase of 50% in intact site and 33% in forested site were evident.

*Figure 7.3: Box plot showing seasonal variability in POC concentrations in all three sites. Fell-Felled, For-Forested, and Int-Intact sites. Horizontal lines in the box are the median POC concentrations; outliers are shown as **



Box plots of POC concentrations for individual sites *(Figure 7.3)* shows that POC concentrations are relatively high during summer months for all sites; however, distinct variability is evident between the sites. Forested site exhibit relatively low variability in POC concentrations compared to the other two sites

(see *Figure 7.3)*. The outliers (shown as *) in all three sites generally occurred during the onset of a stream hydrograph, suggesting abrupt increases in POC concentrations resulted due to increased stream velocity during storm events.

Table 7.4: Season-wise descriptive statistics of POC in mg C L^{-1} for sites

Season	Site	Min	Max	Mean	Std dev	N
SUMMER	*Pooled*	0.0	17.4	2.2 ± 0.1	2.1	464
	Felled	0.0	17.4	2.3 ± 0.2	2.3	172
	Forested	0.0	15.5	1.9 ± 0.2	1.8	128
	Intact	0.0	12.5	2.3 ± 0.2	2.1	164
AUTUMN	*Pooled*	0.0	21.3	2.0 ± 0.7	3.9	29
	Felled	0.5	3.0	1.3 ± 0.3	0.9	10
	Forested	0.0	6.4	1.4 ± 0.6	1.8	10
	Intact	0.5	21.3	3.5 ± 2.2	6.7	9
WINTER	*Pooled*	0.0	6.3	0.9 ± 0.2	1.1	36
	Felled	0.5	6.3	1.6 ± 0.5	1.6	12
	Forested	0.0	1.4	0.6 ± 0.1	0.4	12
	Intact	0.0	1.9	0.6 ± 0.2	0.6	12
SPRING	*Pooled*	0.0	15.8	1.2 ± 0.2	1.7	132
	Felled	0.0	15.8	2.0 ± 0.5	2.9	37
	Forested	0.0	2.3	0.8 ± 0.07	0.5	51
	Intact	0.0	4.2	0.9 ± 0.1	0.8	44

In the intact site, POC concentrations showed a strong positive relationship with flow during all seasons, however, the type of relationship varies across the seasons *(Table 7.5 & Figure 7.4)*. While In the forested site significant linear correlations between POC and discharge during summer (r^2 =0.32, $p<0.001$), autumn and winter (r^2 =0.31, $p<0.05$) months and a poor correlation during spring period are evident *(Table 7.5)*. However, in the felled site the relationship between POC and discharge are very poor.

When POC concentrations are compared against that of DOC, no significant relationships are evident between them. In all sites and at all times,

mean POC concentrations accounted for <10% of the total organic carbon concentrations, except for the intact site during autumn (~14% of TOC).

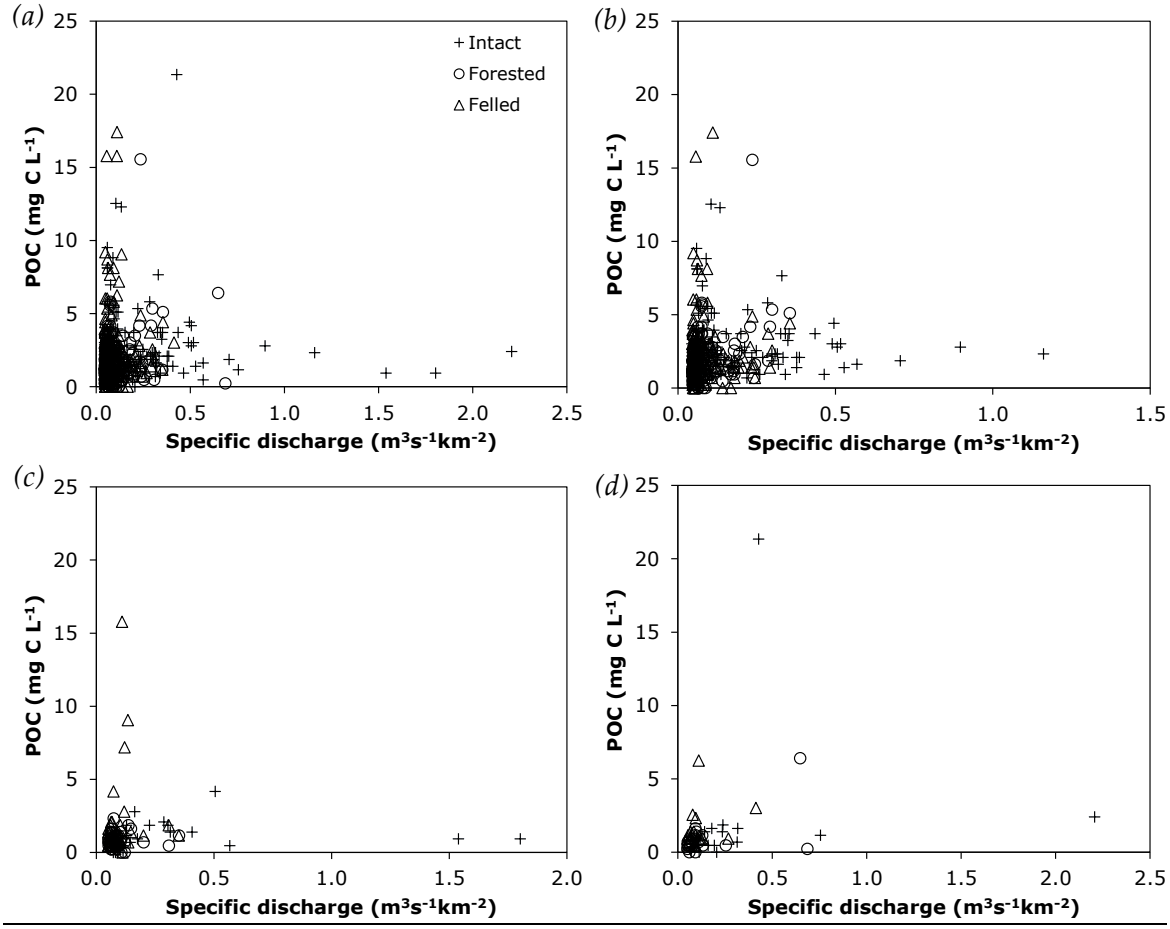


Figure 7.4: Plots showing relationship between POC concentrations, and specific discharge for all three sites. (a) Pooled data (all seasons) (b) Summer, (c) Spring, and (d) Autumn and Winter.

7.6. DOC response during storm episodes

In order to identify the sources and export mechanisms for DOC, understanding the event-scale response of a catchment to precipitation is crucial. Antecedent moisture conditions in a catchment before a rainstorm event will strongly influence the hydrologic flow paths that in turn affect streamwater chemistry (Biron *et al.*, 1999; Worrall *et al.*, 2003; James and Roulet, 2007; Turgeon and Courchesne, 2008). The behaviour of sites during a storm event and the effects of antecedent moisture conditions (e.g. rainfall events after

prolonged dry periods, successive runoff events) are investigated and provided in *Appendix III*.

Hydrological pathways are the main control on DOC concentrations in streamwater (Giusti and Neal, 1993; Wheater *et al.*, 1993; Hinton *et al.*, 1998; Worrall *et al.*, 2002; Inamdar *et al.*, 2004). Therefore, changes in flow pathways during storm events from deeper mineral horizons during low flows to upper organic horizons of peat during high flows deliver most of the DOC found in streams (Billett *et al.*, 2006). Given such a close linkage between soils and stream DOC, it is crucial to identify key flowpaths and delivery mechanisms of DOC to stream waters. Hence, in this section, spatial and temporal variability in the relationship between DOC and stream flow (Q), and possible DOC export mechanisms are investigated.

Spatial and temporal patterns of DOC concentrations in relation to changes in discharge for individual sites are illustrated by time series graphs provided in *Appendix IV*. Variability in DOC concentrations during different runoff events are illustrated in *Figure 7.5 - Figure 7.7*, for individual sites.

In the intact site, a general trend of DOC peak occurring (~0.5 - 8.5 hours) prior to the discharge peak is evident *(Figure 7.5a & c and Table 7.5).* Whereas, in the forested peak DOC concentrations are generally lagged behind the hydrograph peaks by ~1.5 to eight hours *(Figure 7.6a, b & c and Table 7.5)*. Similarly, in the felled site, DOC peaks occur at about four to ten hours after peak discharges *(Figure 7.7a, b & c and Table 7.5)*. However, the variability in DOC with changing discharge is of varying magnitude, depending on the antecedent moisture conditions. One possible explanation for the observed lags in DOC-discharge peaks is the occurrence of DOC hysteresis, which will be discussed in the following section.

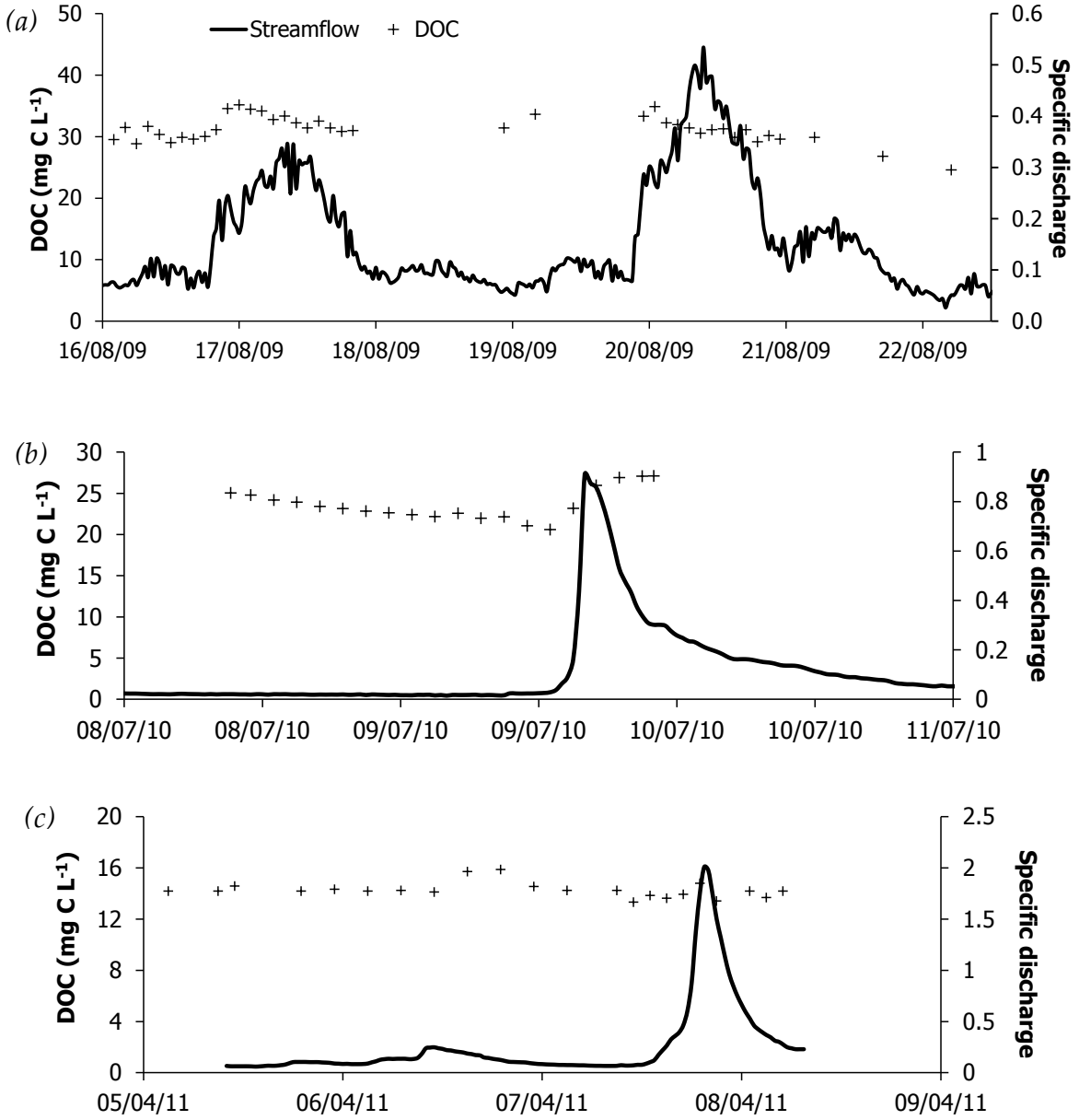


Figure 7.5: Plots showing changes in DOC concentrations related to changes in discharge ($m^3s^{-1}km^{-2}$) in the intact site, during runoff events: (a) August 2009, (b) July 2010, and (c) April 2011.

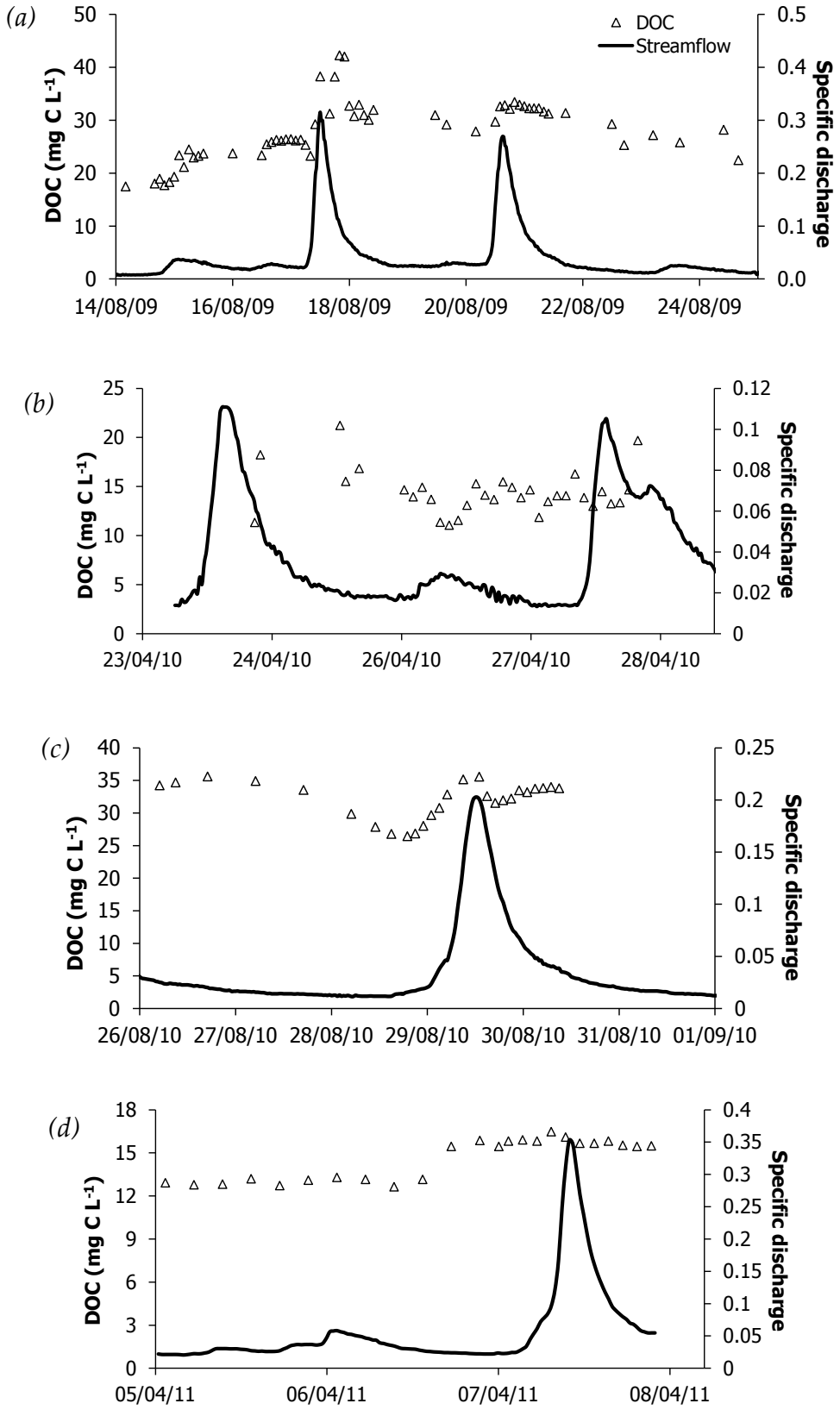


Figure 7.6: Plots showing changes in DOC concentrations related to changes in discharge ($m^3s^{-1}km^{-2}$) in the forested site, during runoff events: (a) August 2009, (b) April 2010, (c) August 2010, and (c) April 2011.

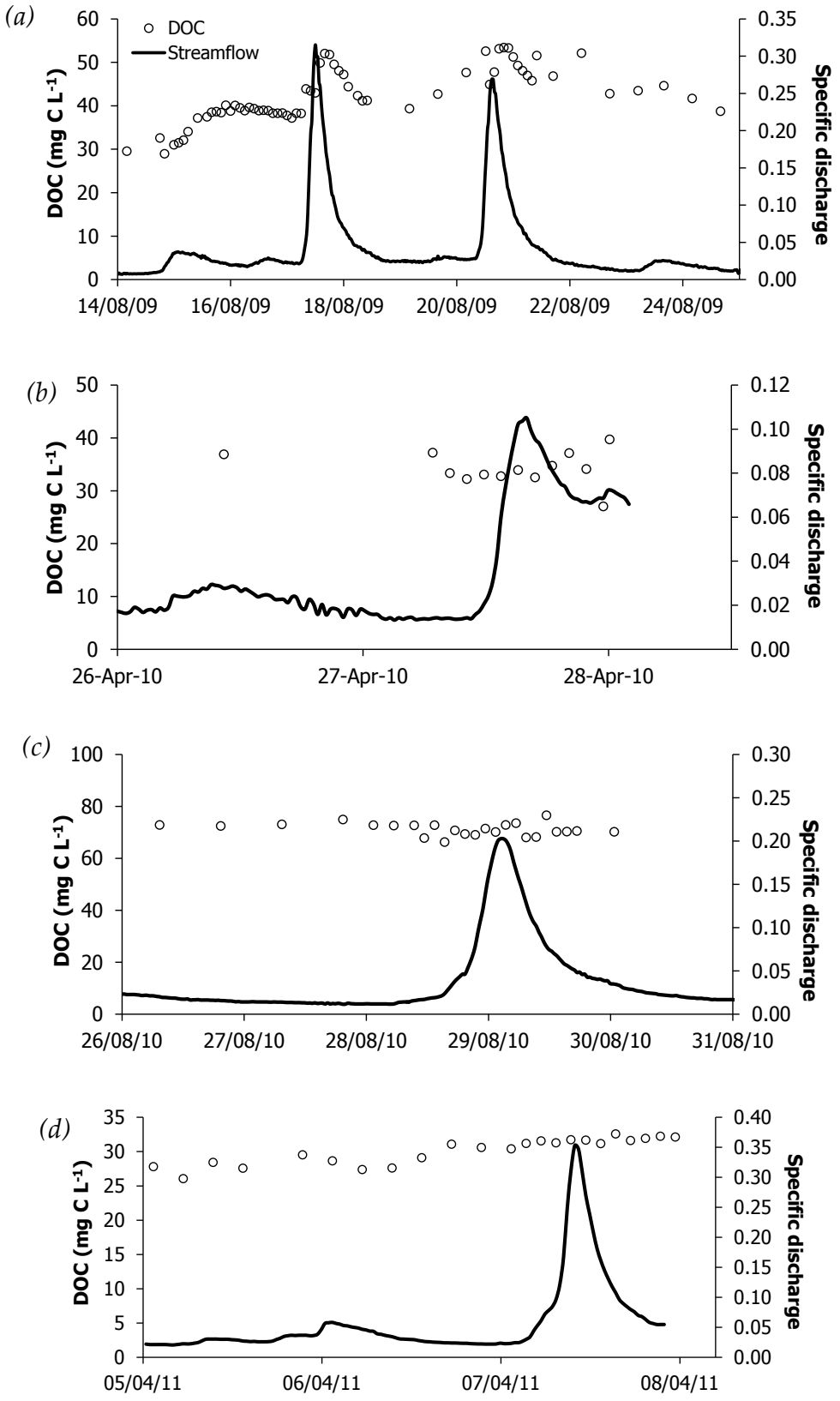


Figure 7.7: Plots showing changes in DOC concentrations related to changes in discharge ($m^3s^{-1}km^{-2}$) in the felled site, during runoff events: (a) August 2009, (b) April 2010, (c) August 2010, and (d) April 2011.

Table 7.5: Peak discharge, DOC concentrations, and lag time between DOC and discharge peaks, during different storm events.

Site	Date	Peak discharge ($m^3\ s^{-1} sq\ km^{-1}$)	Peak DOC (mg C L^{-1})	Lag time (hrs)
INTACT	*17 Aug 2009*	0.34	35.1	7.5 [a]
	20 Aug 2009	0.54	34.9	8.5 [a]
	09 July 2010	0.91	27.0	5.0 [b]
	07 April 2011	2.0	15.0	0.5 [a]
FORESTED	*17 Aug 2009*	0.32	42.2	8.0 [b]
	20 Aug 2009	0.26	33.4	5.0 [b]
	27 April 2010	0.10	20.0	7.0 [b]
	28 Aug 2010	0.20	36.0	1.5 [b]
	07 April 2011	0.35	16.5	2.5 [a]
FELLED	*17 Aug 2009*	0.32	52.0	4.0 [b]
	20 Aug 2009	0.26	53.4	5.0 [b]
	27 April 2010	0.10	40.0	10.0 [b]
	28 Aug 2010	0.20	77.0	10.0 [b]
	07 April 2011	0.35	32.6	5.5 [b]

[a] prior to peak discharge ; [b] after peak discharge

7.7. DOC Hysteresis

Hysteresis occurs where a solute concentration at a given discharge on the rising limb of the hydrograph differs from that at an equivalent discharge on the receding limb (Evans *et al.*, 1999). Determining whether hysteresis occurs, type and direction of hysteresis can in part be used to identify the sources of stream DOC within a given catchment (Evans *et al.*, 1999), as the type of hysteresis is in part governed by the hydrological flowpaths. A minimum of

five samples are needed to define the type of hysteresis (clock-wise or anti-clockwise), as long as the samples are sufficiently represent the rising and receding limb of the stream hydrograph and at or close to the peak discharge (Evans *et al.*, 1999). From *Table 7.5*, it is also evident that lag time is distinct for each site and varies between events, depending on the antecedent moisture conditions in the catchment (James and Roulet, 2007; Turgeon and Courchesne, 2008). However, in a similar study, Evans *et al.* (1999a) found no notable DOC hysteresis, due to the soil type within the catchment. They found that the high DOC concentrations available in organic soil are adsorbed in the mineral horizons resulting in similar concentrations on the rising and falling limbs of the hydrograph.

Therefore, in order to investigate whether or not DOC in the sub-catchments exhibit any hysteresis, and identify the effect of antecedent moisture conditions, DOC concentrations during each runoff event (shown in *Figure 7.5 - Figure 7.7)* are plotted against instantaneous specific discharge as illustrated in *Figure 7.9 - Figure 7.11.*

Intact Site

From the hysteresis loops for the intact site *(Figure 7.9)*, it is evident that of all the events analysed, except for 9 July 2010, DOC concentrations exhibit a clockwise hysteresis *(Table 7.6)*. That is, for each value of discharge on the rising limb, the ratio of DOC to discharge (Q) is greater than that for the same discharge on the falling limb (Williams, 1989). Hence, greater DOC concentrations are measured on the rising limb rather than on the falling limb of the hydrograph at similar discharges.

The widest loops *(Figure 7.9a & d)* indicate relatively larger time gap between the occurrence of DOC and Q peaks (Williams, 1989). In contrast, the narrow loops suggest a decreased time gap between the peaks *(Figure 7.9b & c)*.

The shape of the hysteresis loops *Figure 7.9a, Figure 7.9b &d,* and *Figure 7.9c* are similar to C1, C2, and A3 type loops (respectively) proposed by Evan and Davies (Evans and Davies, 1998) (shown in *Figure 7.8*).

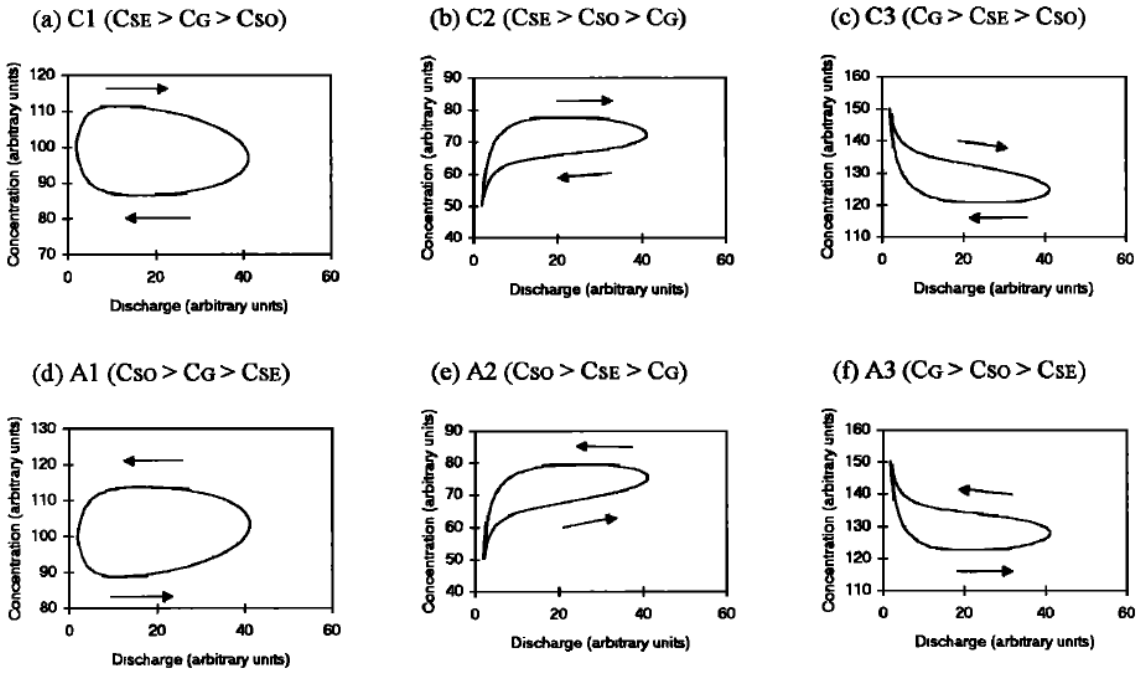


Figure 7.8: Types of hysteresis loops for each combination of source (subscripts: SE-event water, G-groundwater and SO-soilwater) component concentrations, defined by Evans and Davies (1998). C1, C2 & C3 – clockwise rotation; A1, A2 & A3 – anticlockwise rotation.

From *Table 7.6*, it is evident that clockwise rotational pattern is dominant in the intact site, and the loops (C1 and C2 type) suggest that event water is the main source of higher DOC concentrations, with an exception of the event on 9 July 2010 during storm events followed by concentrations from soilwater (or groundwater) component. In contrast, anti-clockwise hysteresis for the event on 9 July 2010 *(Figure 7.9c)* suggests that DOC concentrations from groundwater at the onset of the event give way to soilwater concentrations followed by concentrations from the eventwater towards the receding limb of the hydrograph (A3 type). This is also evident from *Figure 7.5b* where DOC peak occurred on the receding limb of the hydrograph.

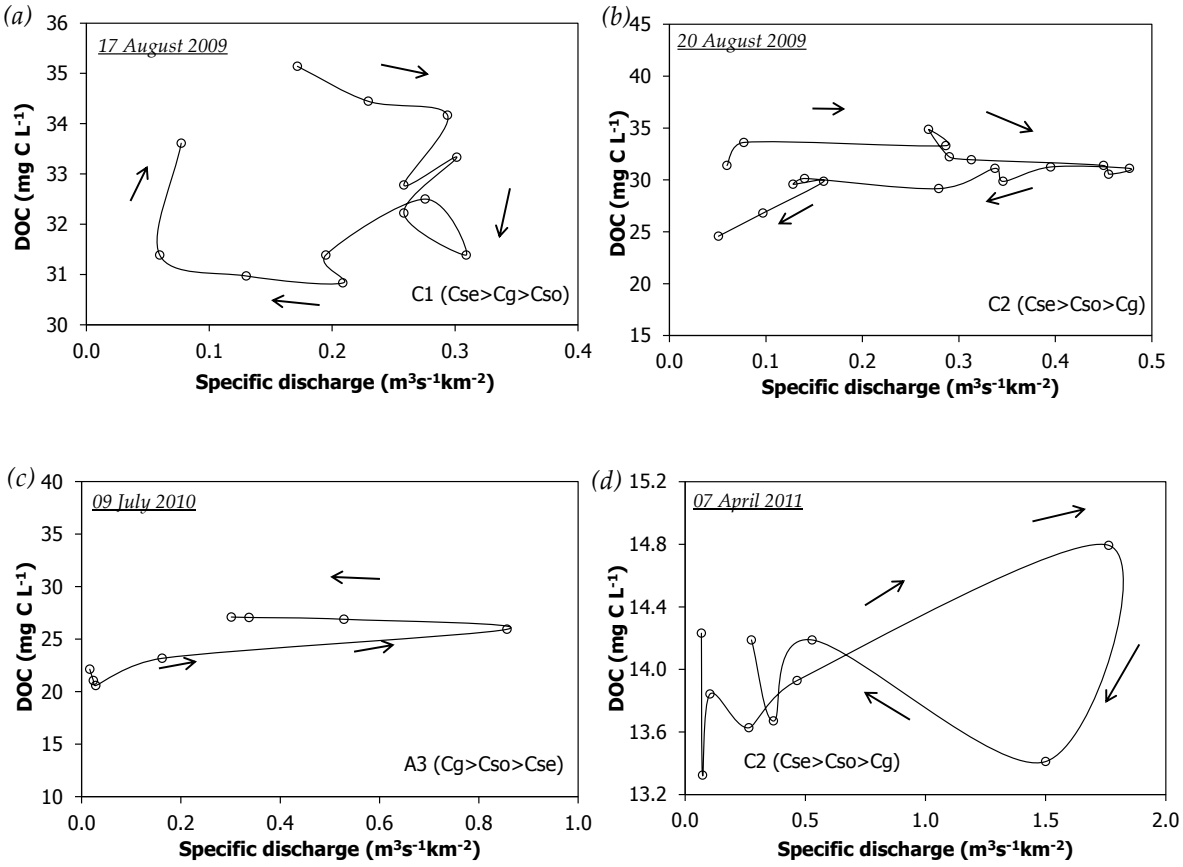


Figure 7.9: Hysteresis loops of DOC and discharge (C-Q plots) for the intact site, during storm events. C1, C2 - clockwise loops, A3 - anticlockwise loop, Cse - event water, Cso - soilwater, and Cg - groundwater DOC concentrations. Note different scales.

Forested Site

From the hysteresis loops for the forested site *(Figure 7.10)*, it is evident that in three of the events analysed, DOC concentrations exhibit anti-clockwise hysteresis *(Table 7.6)*. That is, for each value of discharge on the rising limb, the ratio of DOC to discharge (Q) is lower than that for the same discharge on the falling limb (Williams, 1989). Hence, higher DOC concentrations are measured on the receding limb rather than on the rising limb of the hydrograph at similar discharges.

Anticlockwise hysteresis in this site suggests that DOC peak lags behind the discharge peak, and the A1 and A2 type loops suggest that higher DOC concentrations during an event are mainly input from soilwater sources and are

seen towards receding limb of the hydrograph (Evans and Davies, 1998; Hood *et al.*, 2006). While DOC from groundwater and event water sources appear on the rising limb of the hydrograph. Narrow loops suggest a reduced time gap between DOC and discharge peaks. In the first three events *(Figure 7.10a, b &c)*, soilwater seems to be important in delivering higher DOC concentrations to stream.

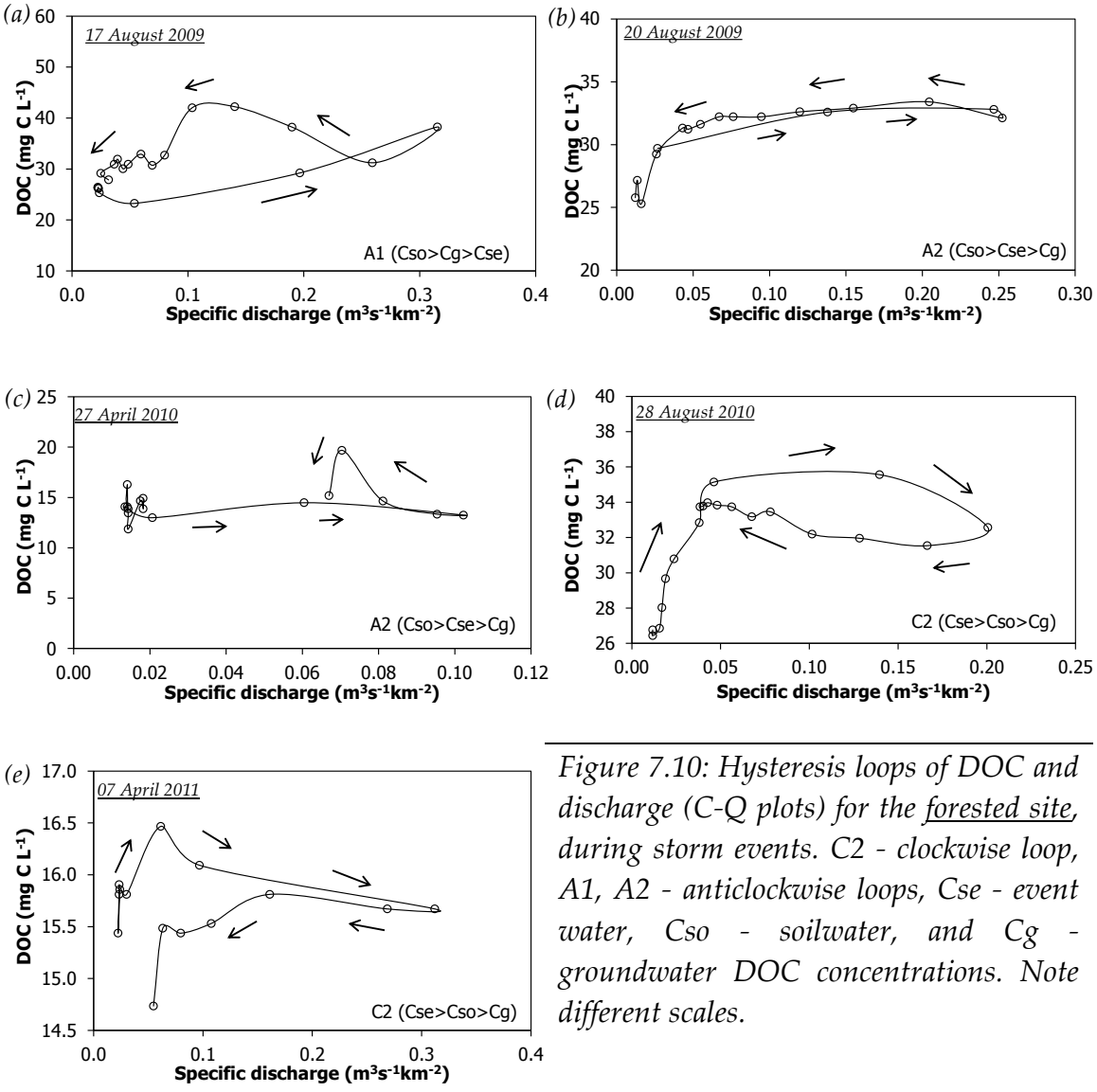


Figure 7.10: Hysteresis loops of DOC and discharge (C-Q plots) for the forested site, during storm events. C2 - clockwise loop, A1, A2 - anticlockwise loops, Cse - event water, Cso - soilwater, and Cg - groundwater DOC concentrations. Note different scales.

During the events on 28 August 2010 and 07 April 2011 *(Figure 7.10d&e)*, clockwise hysteresis loops suggest that DOC concentrations peak before the discharge does, and DOC concentrations from event water dominate the rising

limb of the hydrograph followed by the concentrations from soilwater and groundwater sources as the event progresses.

Table 7.6: DOC hysteresis direction, type of hysteresis loops and source of DOC (based on Evan and Davies, 1998) during storm events

Site	Date	Hysteresis	Type	Source of DOC
INTACT	*17 Aug 2009*	Clockwise	C1	se > g > so
	20 Aug 2009	Clockwise	C2	se > so > g
	09 July 2010	Clockwise	A3	g > so > se
	07 April 2011	Clockwise	C2	se > so > g
FORESTED	*17 Aug 2009*	Anti-clockwise	A1	so > g > se
	20 Aug 2009	Anti-clockwise	A2	so > se > g
	27 April 2010	Anti-clockwise	A2	so > se > g
	28 Aug 2010	Clockwise	C2	se > so > g
	07 April 2011	Clockwise	C2	se > so > g
FELLED	*17 Aug 2009*	Anti-clockwise	A2	so > se > g
	20 Aug 2009	Anti-clockwise	A2	so > se > g
	27 April 2010	Anti-clockwise	A3	g > so > se
	28 Aug 2010	Anti-clockwise	A2	so > se > g
	07 April 2011	Anti-clockwise	A2	so > se > g

se - event water, so - soilwater, and g – groundwater;

Felled Site

In the felled site, all of the events analysed exhibit anti-clockwise hysteresis *(Figure 7.11)*, meaning that maximum DOC concentrations are lagged behind peak discharges. Hence, higher DOC concentrations are seen on the falling limb of the hydrograph rather than on the rising limb of the hydrograph.

Hysteresis loops for this site are predominantly of A2 type, except for an A3 during the event on 27 April 2010.

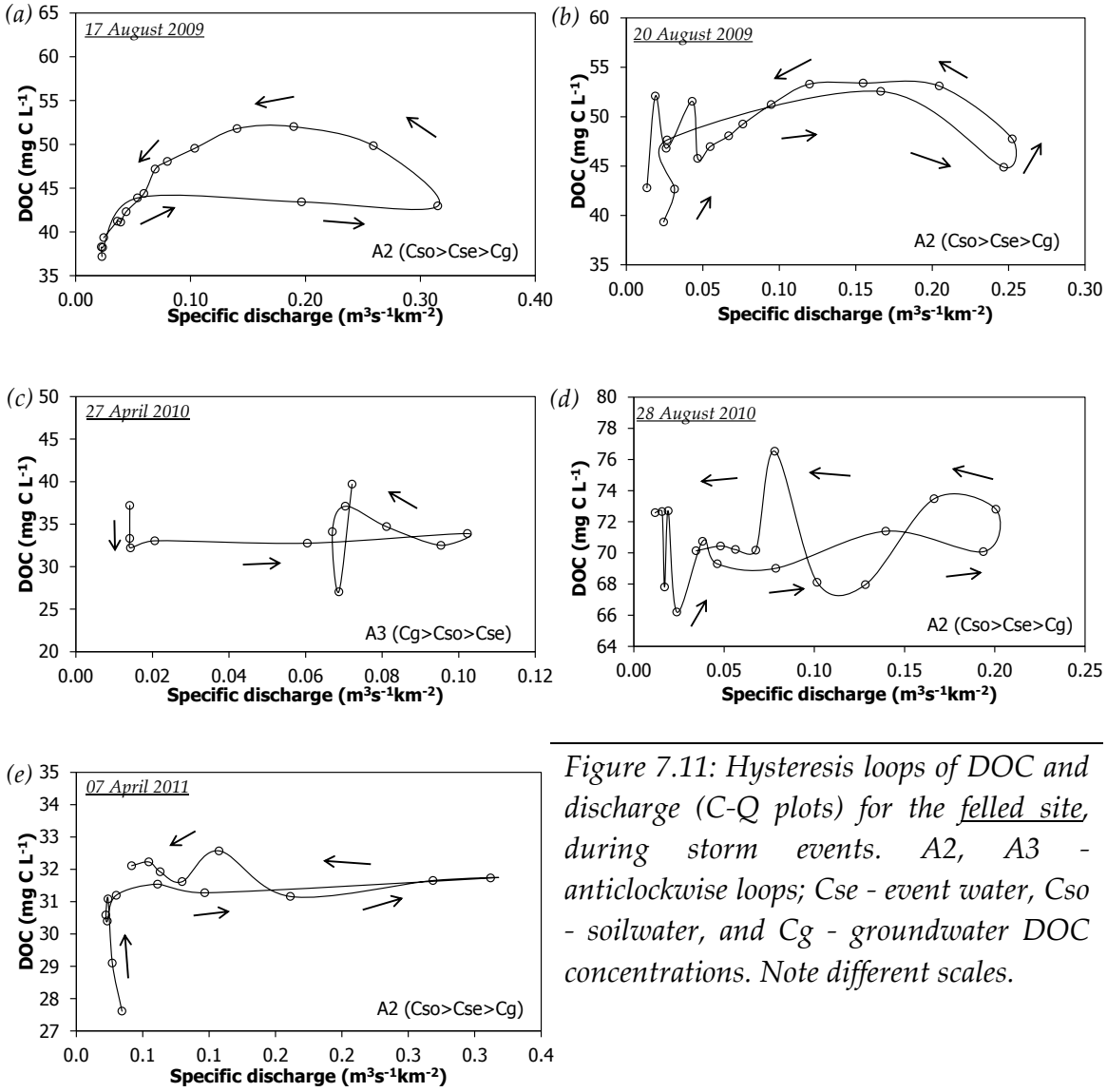


Figure 7.11: Hysteresis loops of DOC and discharge (C-Q plots) for the felled site, during storm events. A2, A3 - anticlockwise loops; Cse - event water, Cso - soilwater, and Cg - groundwater DOC concentrations. Note different scales.

During four of the five studied events *(Figure 7.11a, b, d & e)*, higher DOC concentrations are mainly input from soilwater sources in the later stages of the hydrograph (A2 loops), while concentrations from groundwater and event water dominate during onset and peaks of hydrograph. During the event on 27 April 2010 *(Figure 7.11c)*, DOC concentrations from groundwater dominate during the event giving way to concentrations from soilwater and event water.

7.8. Base cation and metal ion hysteresis

Factor analysis results (see Chapter 6) suggested soilwater source for DOC and metal ions (Fe, Al, Mn and Ti) and groundwater source for weathering derived base cations. In order to see whether or not source of DOC is different to that of base cations and metal ions, and to learn more about the DOC sources and pathways, concentration-discharge (C-Q) analysis was undertaken for Ca, Mg, Fe, and Al. The results for the events from August 2009, and 28 August 2010 (for the felled site) are illustrated for individual sites in *Figure 7.12 - Figure 7.14*.

In the intact site, from *Figure 7.12* it is evident that hysteresis loops of Ca, Mg, Fe, and Al follow the same anti-clockwise rotational direction, which is exactly opposite to that exhibited by DOC *(Figure 7.9a, b* and *Table 7.7)* for the same events. Weathering derived base cations, Ca and Mg exhibit A3 type hysteresis indicating that they are sourced from the same groundwater component. Similarly, Fe and Al show A2 type hysteresis indicating they are mainly sourced from the soilwater component. During a second event (*Figure 7.17e, f, g, & h)* Ca, Mg, Fe, and Al exhibit A3 type hysteresis which indicate mixing of groundwater and soilwater components, and lower concentrations from event water, however, hysteresis direction is again opposite to that of DOC.

In the forested site, from *Figure 7.13 (a, b, c & d)* and *Table 7.7* it is evident that Ca, Mg, and Fe exhibit clockwise hysteresis with higher concentrations occurring on the rising limb of the hydrograph, and the peaks of these solutes occur prior to the discharge peak. Hysteresis direction of these elements is different from that of DOC. During another event *(Figure 7.13e, f, g & h)*, Ca, Mg, and Fe exhibit A3 type hysteresis with lower concentrations occurring on the rising limb and higher concentrations predominantly from groundwater fall on the receding limb. Whereas, Al exhibit an A1 type hysteresis with a primary

source from soilwater component that come during the later stages of hydrograph.

Similarly, in the felled site, the hysteresis of Ca, Mg, Fe *(Figure 7.19)* follow the same rotational direction and C3 type loops suggest a similar source (groundwater). In contrast, Al exhibits anticlockwise hysteresis (A2 and A3 type) suggesting high concentrations from soilwater and groundwater sources *(Table 7.7)*. Hysteresis direction of base cations and metal ions, in this site, are found to be opposite to that of DOC, however, Al shows a similar pattern to that of DOC.

7.9. Soilwater DOC

Soil pore-water samples were collected from tube wells installed at 50cm, 100cm and 150cm depths to tap soilwater from 30-50cm, 80-100cm and 130-150cm respectively. These samples were filtered and analysed for absorbance and DOC using a similar procedure followed for streamwater samples. Details of sample collection and analysis are provided in Chapter 4.

The magnitude and range of DOC concentrations, pH, and absorbance (E_4/E_6) values observed vary considerably from site to site as shown in *Figure 7.15 & Figure 7.16*. pH ranged from 4.0 to 6.1 units at 50cm depth, from 5.5 to 6.9 units at 100cm and about 4.7 to 7.1 units at 150cm depth *(Figure 7.16a)*. Increase in pH values is observed with increasing depth in all the sites, reflecting the influence of bedrock weathering in deeper horizons.

Soilwater DOC concentrations varied substantially from site to site and with increasing depth in peat, an increase in the concentrations up to a depth of 100cm and then a decline in concentrations at a depth of 150cm are evident from *Figure 7.15b.*

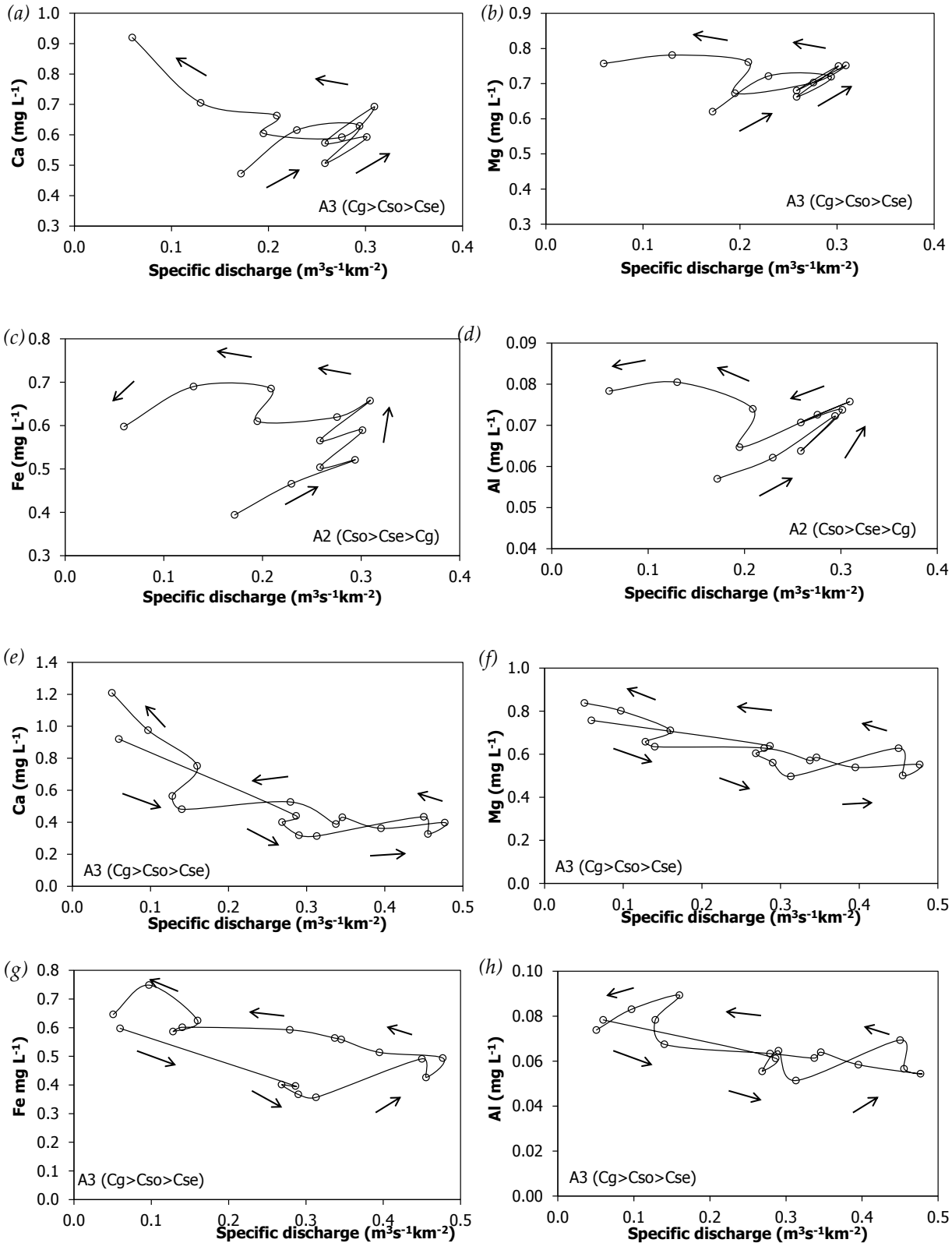


Figure 7.12: C-Q plots of Ca, Mg, Fe, Al for the intact site, during the runoff events: a,b,c,and d - 17 August 2009; e,f,g, and h - 20 August 2009. A2, A3 - anticlockwise loops; Cse - event water, Cso - soilwater, and Cg - groundwater DOC concentrations. Note different scales.

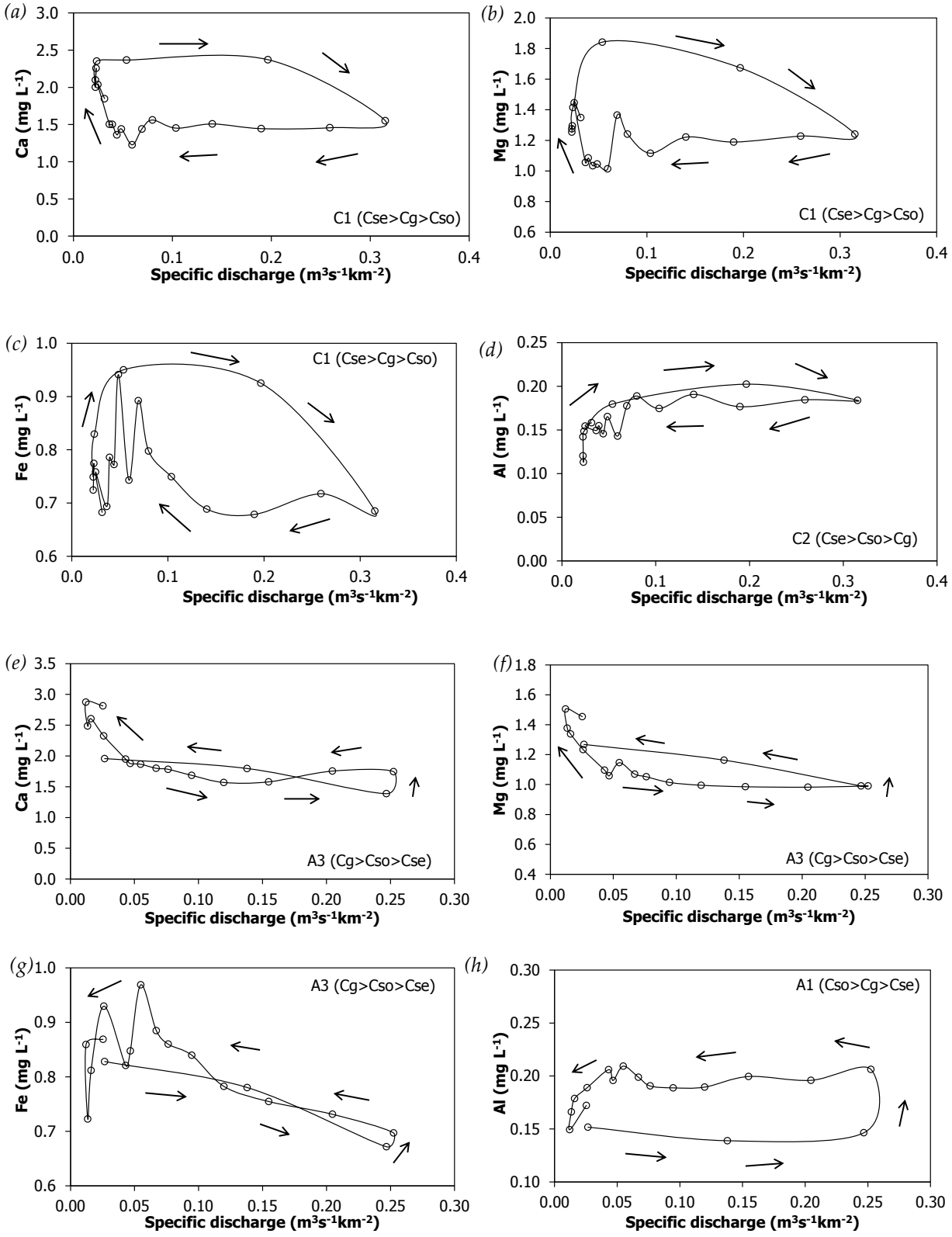


Figure 7.13: C-Q plots of Ca, Mg, Fe, Al for the forested site, during the runoff events: a, b, c, and d - 17 August 2009; e, f, g, and h - 20 August 2009. C1, C2 – clockwise loops; A1, A3 - anticlockwise loops; Cse - event water, Cso - soilwater, and Cg - groundwater DOC concentrations. Note different scales.

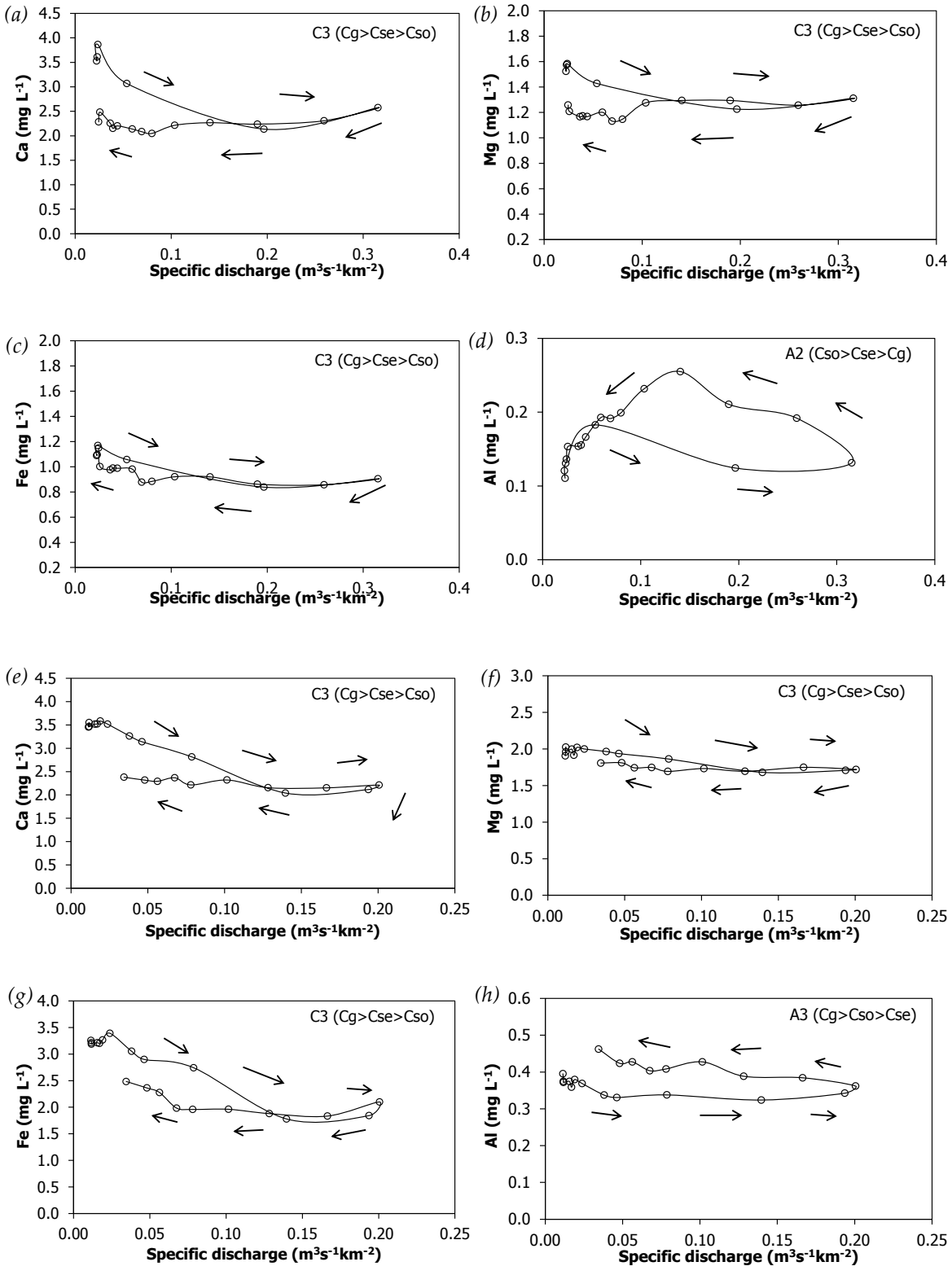


Figure 7.14: C-Q plots of Ca, Mg, Fe, Al for the felled site, during the runoff events: a, b, c, and d - 17 August 2009; e, f, g, and h - 28 August 2010. C3-clockwise loop, A2, A3 - anticlockwise loops; Cse - event water, Cso - soilwater, and Cg - groundwater DOC concentrations. Note different scales.

Table 7.7: A comparison of DOC, metal ion and base cation hysteresis: direction, type of loops and possible sources (based on Evan and Davies, 1998) during two summer storm events.

Site		Hysteresis direction	Type	Source
INTACT	*DOC*	Clockwise	C1, C2	se > g > so, se > so > g
	Ca	Anti-clockwise	A3	g > so > se
	Mg	Anti-clockwise	A3	g > so > se
	Fe	Anti-clockwise	A2, A3	so > se > g, g > so > se
	Al	Anti-clockwise	A2, A3	so > se > g, g > so > se
FORESTED	*DOC*	Anti-clockwise	A1, A2	so > g > se, so > se > g
	Ca	Clockwise, Anti-clockwise	C1, A3	se > g > so, g > so > se
	Mg	Clockwise, Anti-clockwise	C1, A3	se > g > so, g > so > se
	Fe	Clockwise, Anti-clockwise	C1, A3	se > g > so, g > so > se
	Al	Clockwise, Anti-clockwise	C2, A1	se > so > g, so > g > se
FELLED	*DOC*	Anti-clockwise	A2	so > se > g
	Ca	Clockwise	C3	g > se > so
	Mg	Clockwise	C3	g > se > so
	Fe	Clockwise	C3	g > se > so
	Al	Anti-clockwise	A2, A3	so > se > g, g > so > se

se - event water, so - soilwater, and g – groundwater

Such decreasing trends in DOC and increasing trend in pH with varying depths were reported in similar studies (Grieve *et al.*, 1995; Wallage *et al.*, 2006; Clark *et al.*, 2007). Of all three sites, soilwater DOC concentrations in the forested site show relatively lower concentrations, while that from intact site show relatively high variability.

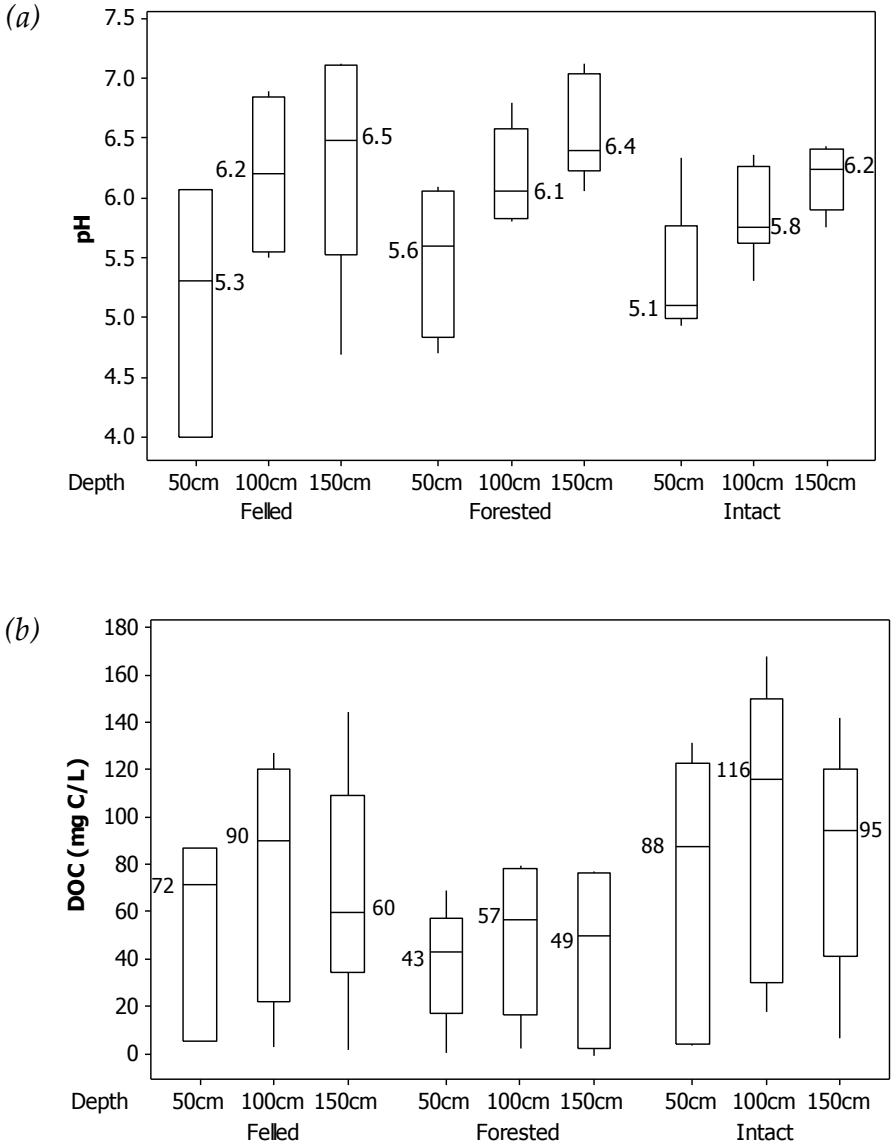


Figure 7.15: Box plots showing changes in pH and DOC concentrations with increasing depth. (a) pH increases with depth; (b) DOC concentrations increase at 100cm depth and then decrease with increasing depth. Median values of pH and DOC are shown on the plots.

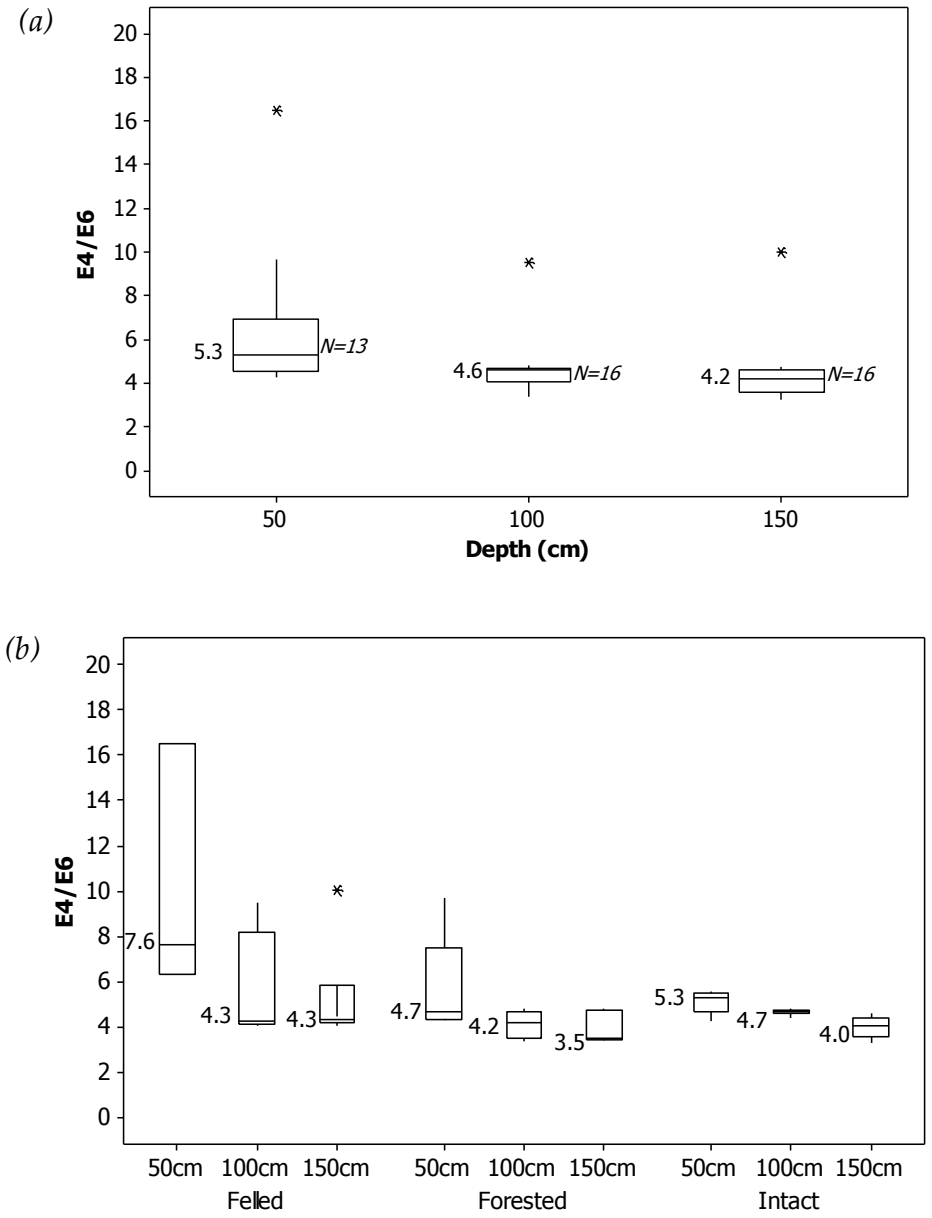


*Figure 7.16: Box plots showing changes in values with increasing depth. (a) Pooled data, (b) Site-specific. Median E_4/E_6 values are shown on the plots. Outliers shown as *.*

E_4/E_6 ratio determined using the absorbance at 465 nm (E_4) and 665 nm (E_6) indicate relative humification of peat (Thurman, 1985; Worrall *et al.*, 2002; Wallage and Holden, 2010). The dominance of more mature humic acids in DOC implies high low E_4/E_6 value and enrichment of less mature or relatively young fulvic acids in DOC is reflected by a higher E_4/E_6 value; this ratio range between 2-5 for mature humic acids and between 8 - 10 for fulvic acids

(Thurman, 1985). E_4/E_6 values in soilwater at different depths for individual sites are illustrated by box plots in *Figure 7.16.* A decrease in the E_4/E_6 ratio with increasing depth is evident from pooled data and in individual sites *(Figure 7.16a & b)*. A similar decrease in this ratio was reported by Wallage *et al.* (2006), they have divided the peat into two distinct layers based on the E_4/E_6 ratio: an upper layer (high E_4/E_6 ratio) dominated by fulvic acids and a lower layer (low E_4/E_6 ratio) enriched in mature humic acids.

From *Figure 7.16b*, it is apparent that DOC is relatively young (6.3 - 16.5) in the upper layers (< 50cm) of peat in the felled site compared to the other sites, which may be derived from the decomposition of litter of recently felled trees. The E_4/E_6 ratio in the shallow peat (< 50cm), range from 4.3 - 9.7 in the forested site, and from 4.25 - 5.6 in the intact site. Hence, DOC in the shallow peat layers at the intact site seems relatively mature compared to that in the forested and felled sites where a constant supply of fresh organic matter in the form of leaves, twigs or litter from felled trees is added regularly.

7.10. E_4/E_6 in stream water during storm events

Variability in E_4/E_6 ratio due to the changes in discharge, during storm events, is illustrated in *Figure 7.17- Figure 7.19* for each individual site. From the E_4/E_6 pattern in the graphs, it is apparent that, irrespective of landuse in the sub-catchments, high E_4/E_6 values (>7 for the forested and felled sites, and >6 for the intact site) are associated with high DOC concentrations *(*see *Figure 7.5- Figure 7.7)* confirming that most of the DOC exported during the storm events is relatively younger. On the other hand, it is evident from the graphs that relatively mature DOC (low E_4/E_6) is generally associated with peak discharges, suggesting the dominance of water inputs from deeper peat horizons during the high stream flows.

When the E_4/E_6 values during DOC peaks are compared to their ranges at different depths in a given site, values strongly coincide and range within those from 30 - 50cm depth. Since there is no data available for depths < 30cm, this study does not consider the DOC source from the shallower depths (0-30cm). However, the results obtained are consistent with that from similar studies (Wallage *et al.*, 2006; Clark *et al.*, 2008), hence, it can be confirmed that most of the DOC during storm events come from peat layers not deeper than 50cm depth.

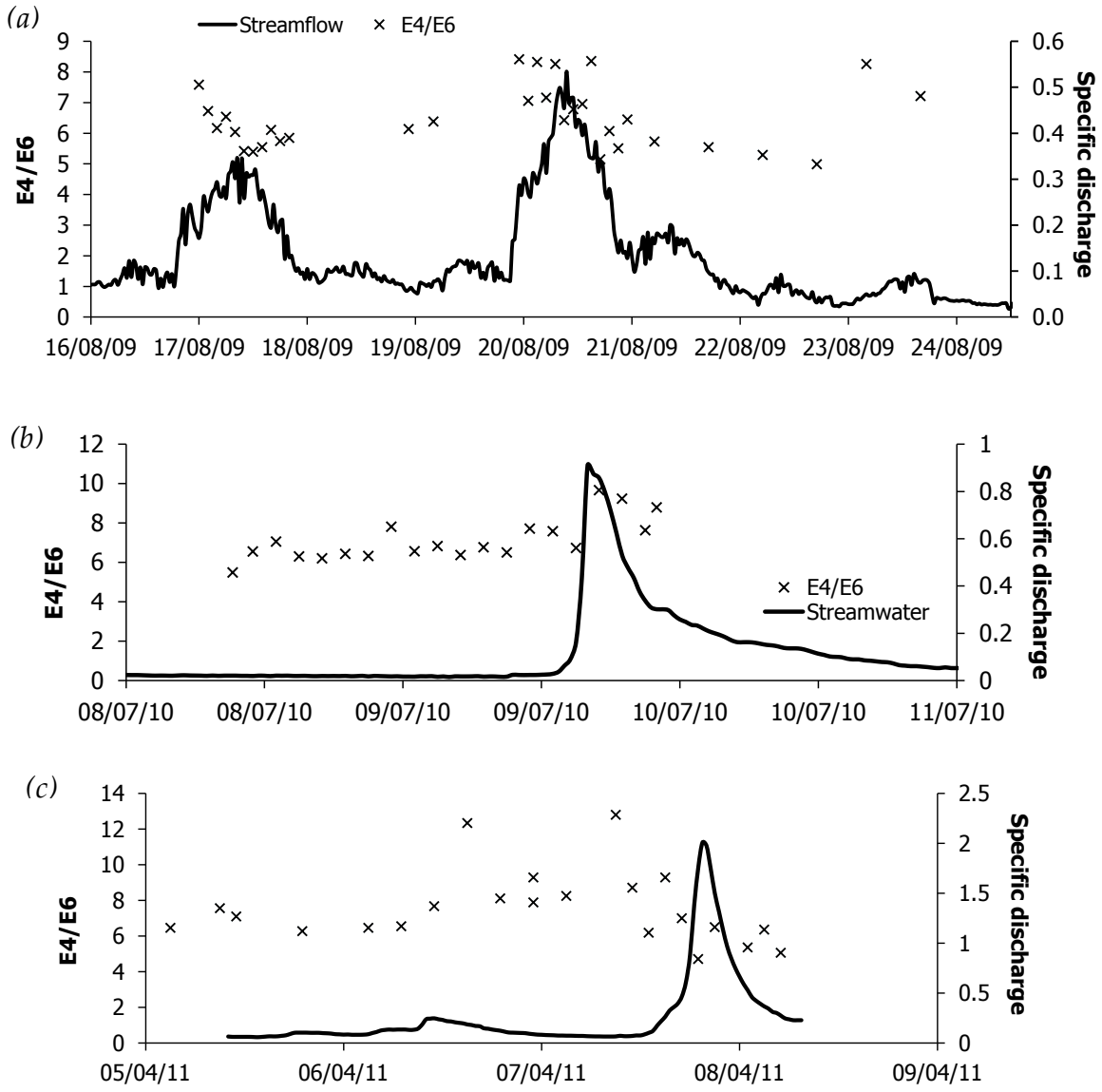


Figure 7.17: Plots showing changes in E_4/E_6 ratio related to changes in discharge in the intact site, during storm events: (a) August 2009, (b) July 2010, and (c) April 2011.

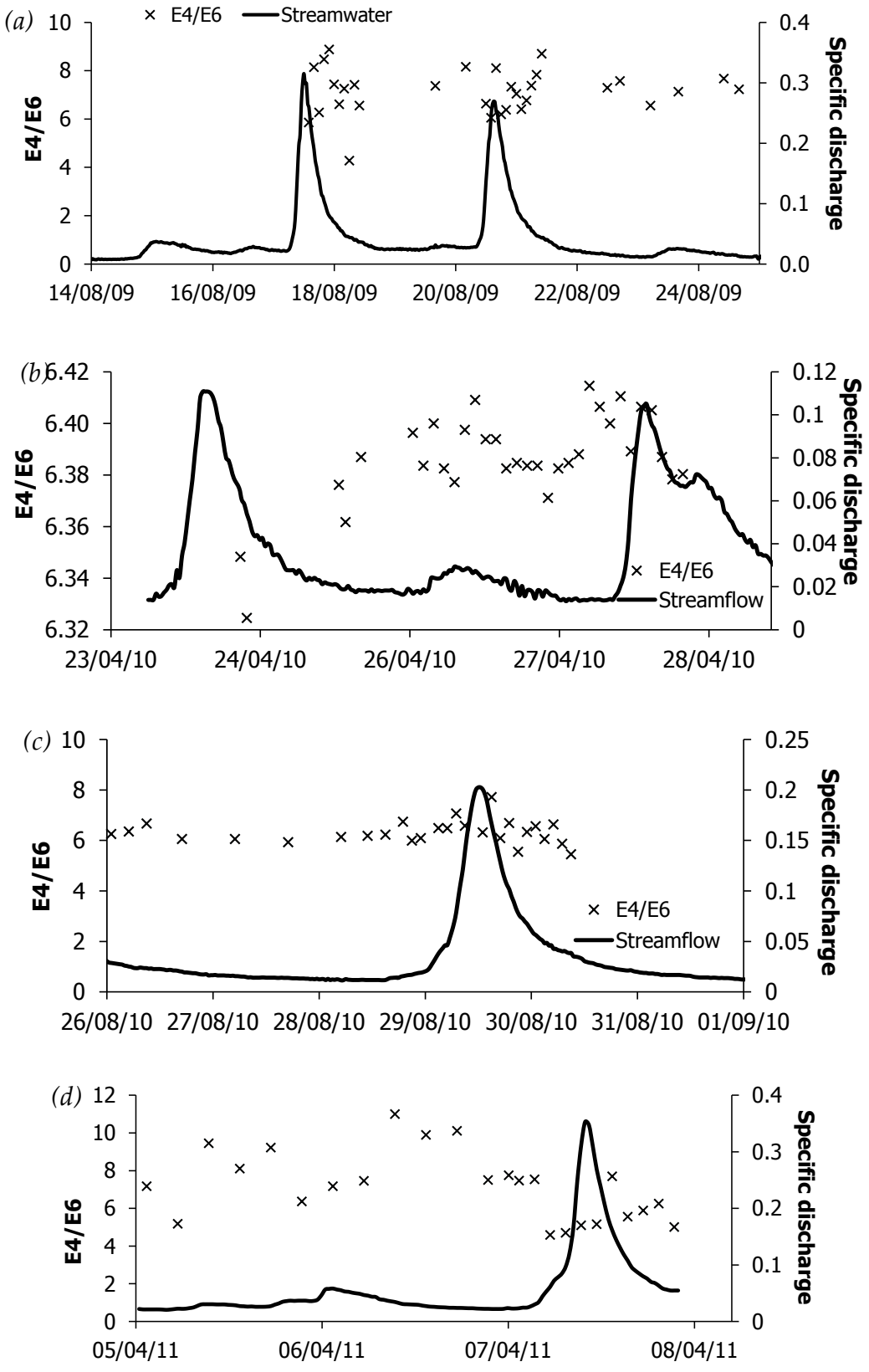


Figure 7.18: Plots showing changes in E_4/E_6 ratio related to changes in discharge in the forested site, during storm events: (a) August 2009, (b) April 2010, (c) August 2010, and (c) April 2011.

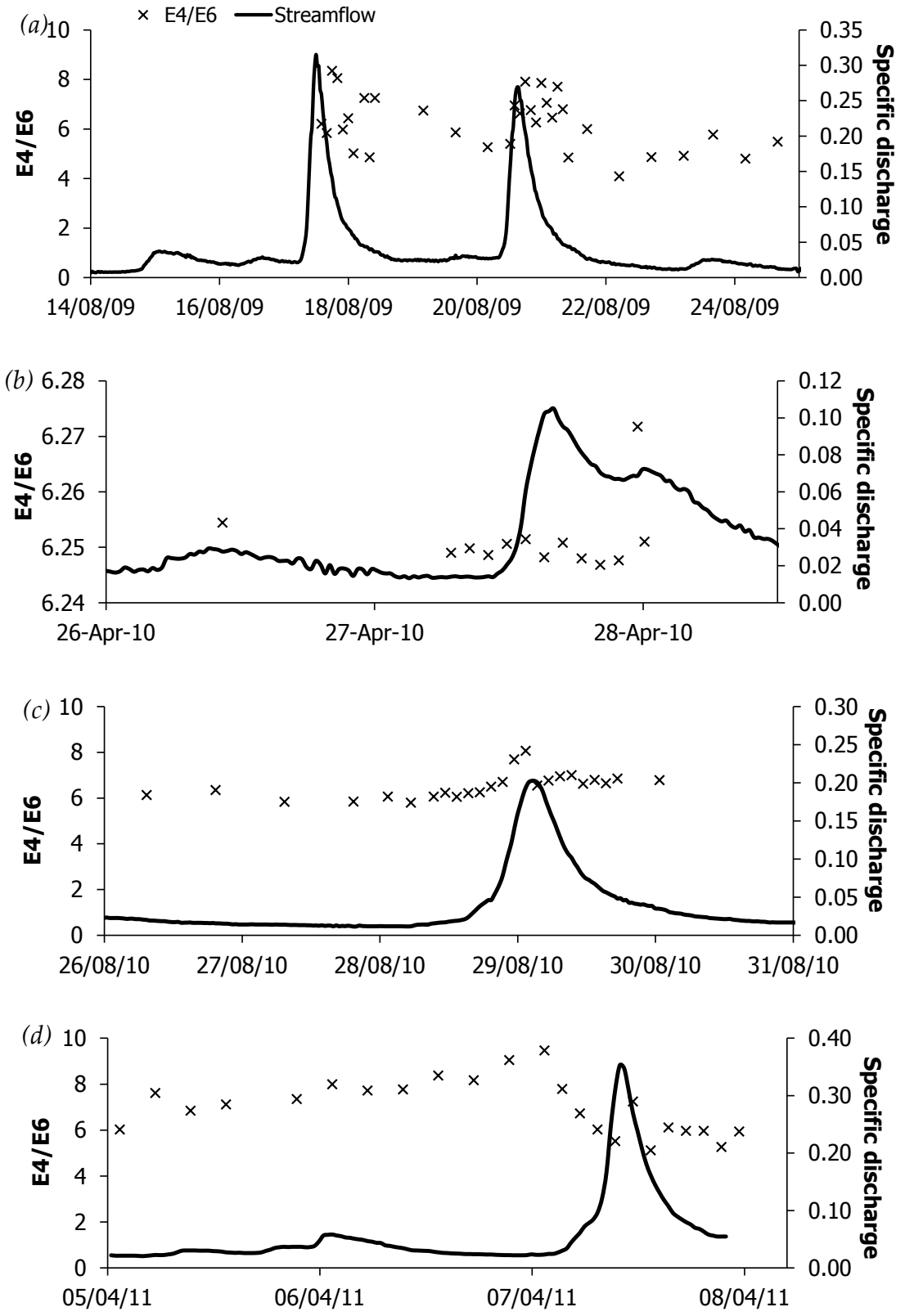


Figure 7.19: Plots showing changes in E_4/E_6 ratio related to changes in discharge in the felled site, during storm events: (a) August 2009, (b) April 2010, (c) August 2010, and (d) April 2011.

7.11. Discussion

In this chapter it has been attempted to: i) investigate the changes in dissolved organic carbon related to changes in stream discharge, ii) identify the major flowpaths through which DOC is exported to streams, and iii) investigate the export mechanisms of DOC. Summer and spring storm events where relatively intense DOC data are available were analysed to identify major flowpaths of DOC, however, winter and autumn samples (spot samples) were used to understand the variability of DOC with changing discharge.

Streamwater DOC concentrations in the catchment are observed to be high during summer storm events and followed by that during spring storm events *(Table 7.4)*. This may be due to the higher rates of DOC production with increasing temperatures, which is eventually released due to increased flow through the soil matrix during the spring and summer storm events (Freeman *et al.*, 2001; Dawson *et al.*, 2008; Worrall *et al.*, 2008; Clark *et al.*, 2009). A decline in DOC concentrations observed during autumn indicates exhaustion of available DOC produced during summer months. A further drop in DOC concentrations during winter months is possibly indicative of reduced rates of DOC production due to low temperatures and/or effect of snowmelt. Of all the three sites, high DOC concentrations and relatively high variability in concentrations occur in the felled site, where the decomposition of felled trees is possibly a major contributor of DOC. Concentrations and variability of DOC are minimum at the intact site and relatively intermediate at the forested site. Such spatial and temporal variability observed in DOC concentrations, in the catchment, appears to be a function of hydrological processes interacting with the biogeochemistry of terrestrial and aquatic ecosystems (Hornberger *et al.*, 1994; Lohse *et al.*, 2009; Dawson *et al.*, 2011).

Similar to DOC, particulate organic carbon (POC) concentrations in all the sites exhibit seasonality suggesting different sediment transportation rates with

respect to changing flow intensities at different seasons of a year *(Figure 7.3)*. POC concentrations vary spatially in the catchment, highest POC concentrations are transported from the intact site followed by that from the felled and the forested sites. Increased POC concentrations are generally associated with summer storm events, which could be due to the increase in river energy to transport particulate matter during high intense summer storms. Such increase in POC could be indicative of enhanced peat erosion during summer months, because abrupt changes in flow during storm events can erode the peat delivering POC and sediment to streams (Holden and Burt, 2003; Holden, 2006). Relatively low POC concentrations and low variability in the felled site could be due to the drain blocking techniques (as a part of restoration), which reduce rapid runoff (Holden, 2005; Holden *et al*., 2007) from this site. No significant relationship between DOC and POC concentrations was evident from the data, however, POC accounted for 7 - 9% of the total organic carbon (DOC and POC) in streamwaters from each site. Therefore, streamwater organic carbon from River Dyke catchment is mainly DOC dominated.

Relationship between DOC and discharge

A distinct seasonality in the relationship between DOC concentrations and discharge (Q) was evident from the results *(Table 7.5)*, stronger relationship are associated with summer, autumn and winter periods, and relatively weaker relationships during spring season suggest a different control than discharge on DOC concentrations. Seasonality explains about 10 - 68% variation in the data, which is similar to that demonstrated by Clark *et al.* (2008) and Miller *et al.* (2001). Unexplained relationship between DOC and discharge could be due to: i) at low flows - wide range of DOC concentrations resulting from groundwater contributions during dry periods and from lowflows immediately following an event. ii) at high flows - DOC concentrations that generally increase initially

with increasing discharge, instead of increasing with flow (Hope *et al.*, 1994), tend to decline as the event progresses (inverse relationship). This is perhaps due to the DOC-rich water in the acrotelm is diluted by rainwater with low DOC concentrations (Worrall *et al.*, 2002; Clark *et al.*, 2007) which nullifies the positive correlation from the earlier stages of the hydrograph, resulting in a poor DOC-Q correlation. This interpretation is well supported by the DOC hysteresis demonstrated in *Section 7.7*.

A general trend of DOC hysteresis observed in the intact site is DOC peaking prior to the discharge peak, whereas in the forested and felled sites, it is DOC peak lagging behind that of discharge. However, the lag time between peaks of DOC and discharge appears to be a function of antecedent moisture conditions in the catchment (Biron *et al.*, 1999; James and Roulet, 2007; Turgeon and Courchesne, 2008). The findings from hysteresis analysis are in agreement with those from the end-member mixing analysis (EMMA) model for the respective storm events. Therefore, in the intact site, the occurrence of C1, C2 and A3 hysteresis types suggest that event water peaks before pre-event water (Evans and Davies, 1998). This means that the water entering the stream during the early part of the hydrograph had higher DOC concentrations compared to water entering stream during later stages of the event (Hood *et al.*, 2006). Additionally, C1 and C2 type loops in the intact site suggest DOC flushing, generally following dry antecedent conditions (Soulsby, 1995; Evans and Davies, 1998).

A close comparison of DOC variability from the forested and felled sites reveals that the DOC patterns (not the concentrations) during runoff events are very similar in both the sites; however, DOC response times vary slightly given the different landuse. In both these sites, a general pattern observed is one of a 'lag in DOC peaks', while a 'lag in discharge peaks' is common in the intact site. Lagging of event water behind pre-event water, in these sites suggests that

higher DOC concentrations are coming from relatively farther places in the catchment to stream. Predominance of A2 type loops in both the sites suggest that the DOC concentrations in the initial stages of the event are low and as the water inputs are mainly from the riparian groundwater and/or deep soilwater (termed as 'pre-event water) nearer to the stream. As the event progresses, this pre-event water is displaced by the event water and is moved to the stream (Evans and Davies, 1998; Inamdar *et al.*, 2004; Hood *et al.*, 2006). In addition, during this process eventwater moving through the soil (from the farther areas in the catchment) tend to establish hydrological connectivity in the catchment and access wider areas of DOC stores available in the catchment (Inamdar *et al.*, 2004), as reflected by high DOC concentrations on the receding limbs of the hydrograph in both the sites.

Similarly, during an event following wet-antecedent moisture conditions in the catchment, water table (or hydrological connectivity) that has been already high increases readily in response to even a low magnitude rainfall. Consequently, flowpaths may change and shallow-subsurface or surface flow may predominate; however, in such conditions, where available DOC already being flushed or exhausted during an earlier event, a dilution or relatively low DOC concentrations are generally seen, which can be observed in the forested and felled sites during the events on 20 Aug 2009 and 27 April 2010. Therefore, length of the time since the previous storm event is one of the important controls on DOC concentrations measured in streamwater (Worrall *et al.*, 2002).

On comparing the hysteresis of metal ions and base cations with that of DOC, it was found that: i) source of DOC in the intact site appears to be different from Ca, Mg, Fe, and Al, ii) in the forested site source of Ca, Mg, Fe is groundwater, while that of Al and DOC is mainly soilwater; and iii) in the felled site, groundwater is the main source of Ca, Mg, and Fe, while it is soilwater and eventwater for DOC and Al.

These findings are consistent with factor analysis results, which delineated the source of weathering derived Ca, Mg, K, and Na as groundwater and that for Fe, Al, Mn, Ti and DOC as soilwater. Occurrence of Fe with Ca and Mg is suggestive of reductive solution of Fe oxides and hydroxides at increasing depths at low redox conditions (Abesser *et al.*, 2006). Despite the C-Q analysis suggesting a similar source for DOC and Al, on comparing the shape of hysteresis loops, it is evident that there exists a slight difference in the source (within the soilwater component) between these two species; however, this has been addressed by depth related information (soilwater data) of DOC concentrations.

Connection between soilwater, streamwater DOC and hydrological flow paths

In this study, DOC concentrations and absorbance tend to increase up to a certain depth (100cm) and then decrease (Wallage *et al.*, 2006) further downwards (>100cm), and this is true for all sites, which could be due primarily to sorption processes in mineral soils (Hinton *et al.*, 1998; Billett *et al.*, 2006).

Results from the factor analysis and end-member mixing analysis (EMMA) has already confirmed that soilwater component is a primary source of DOC and associated metal ions (Fe, Mn, and Al) (see *Chapter 6*). Hence, increase in streamwater DOC concentrations and absorbance, observed during storm events reflect a switch in the dominant end-members from less acidic relatively low DOC water (groundwater) to acidic DOC rich waters, with storm flow diluted by low DOC rainfall inputs (Worrall *et al.*, 2002; Soulsby *et al.*, 2003; Clark *et al.*, 2007, 2008). However, DOC hysteresis analysis results suggest a source slightly different for DOC from that of Fe, Mn and Al within the same soilwater component. Subsequently, the E_4/E_6 ratio analysis results suggest that shallow subsurface flow in the upper peat layers is the primary flow path that

provides the majority of DOC to stream flow during storm events (Boyer *et al.*, 1997); thus exported DOC is relatively young and coming mainly from the near - surface (<50cm) horizons of peat (Billett *et al.*, 2007). In addition, these results confirm similar findings based on soilwater and streamwater hydrochemistry, linking near-surface (relatively young) DOC to that delivered into streamwaters (Boyer *et al.*, 1997; Schiff *et al.*, 1997; Palmer *et al.*, 2001; Billett *et al.*, 2006, 2007; Clark *et al.*, 2008), and disconnection between older DOC ($E_4/E_6 < 4$) in the lower peat layers (>100cm depth) and streamwater (Billett *et al.*, 2006; Worrall *et al.*, 2006b).

Of all sites, relatively lower DOC concentrations in streamwater and higher concentrations in soilwater in the intact site, probably suggest that this site has a relatively larger C pool and only a small fraction of this stored carbon pool is contributing DOC losses from this site (Billett *et al.*, 2006). Moreover, based on E_4/E_6 ratio range, intact site seems to have relatively more mature DOC compared to that in the other sites. DOC in the forested and felled sites is relatively young or less mature as a constant supply of fresh organic matter (leaves, twigs or litter from felled trees) is added regularly to C pool in these sites.

Hydrological pathways and export mechanisms of DOC

In the forested catchments, significant volumes of pre-event water are stored in the near-stream zone and are available for rapid displacement in the next event (Stewart and McDonnell, 1991; Turgeon and Courchesne, 2008). Eventually, during storm events, infiltrating event water moves rapidly to depth via macropores (roots zones, peat pipes etc), and a saturated zone develops at deeper horizons that mix up with stored pre-event water before moving towards the stream channel (Burt and Pinay, 2005). This perhaps may be the reason for the observed co-occurrence of Ca, Mg, Fe, and Mn peaks at the onset of runoff events, in the forested and felled sites. During this process,

lateral movement of infiltrated water with relatively longer residence times to access available DOC in the shallow layers of peat leads to the observed lag in DOC peaks.

Therefore, in the forested and felled sites, subsurface flow generated by rapid flow (of event water) through macropores is responsible for peak discharges, while that through soil matrix or a mixture of rapid flow and soil matrix flow appear to be responsible for the observed DOC peaks. On the other hand, in the intact site, shallow subsurface flow of eventwater appears to be predominant during runoff events, while riparian zones do not dominate the nature of the stream discharge (Worrall *et al.*, 2002).

Conceptual models

Based on the evidence from spatial and temporal variability in streamwater chemistry, and integrating the findings from end-member mixing, DOC, metal ion and base cation hysteresis, and E_4/E_6 ratio analyses, conceptual models explaining catchment response and evolution of DOC during summer/spring storms is proposed. This model is classified into four stages representing varying stages of stream hydrograph. Since the mechanisms differ between the intact and the forested and felled sites, two different models are proposed *(Figure 7.20 & Figure 7.21)*.

It was assumed that prior to an event, under base flow conditions, water low in DOC concentrations from deeper soil horizons with limited available carbon is the primary source to streams (Jones and Mulholland, 2000; Fitts, 2002).

Intact Site

Stage 1*: Early stages of the rising limb of hydrograph (Figure 7.20a).* As the rainwater infiltrates, watertable rises and percolation excess water, accessing

DOC stores in the shallow subsurface, is delivered to stream. DOC concentrations begin to rise.

Stage 2: *Rising limb of the hydrograph (Figure 7.20b).* As the event progresses, lateral moving event water rich in DOC, flushes the available DOC in the acrotelm, hence higher DOC concentrations occur at this stage.

Stage 3: *Peak discharge (Figure 7.20c).* Saturation excess runoff or shallow subsurface flow depleted in DOC mixes up with soilwater from deeper sources (with relatively longer residence times) rich in ions such as Fe, Mn, Al, and Ti dominate the stream flow.

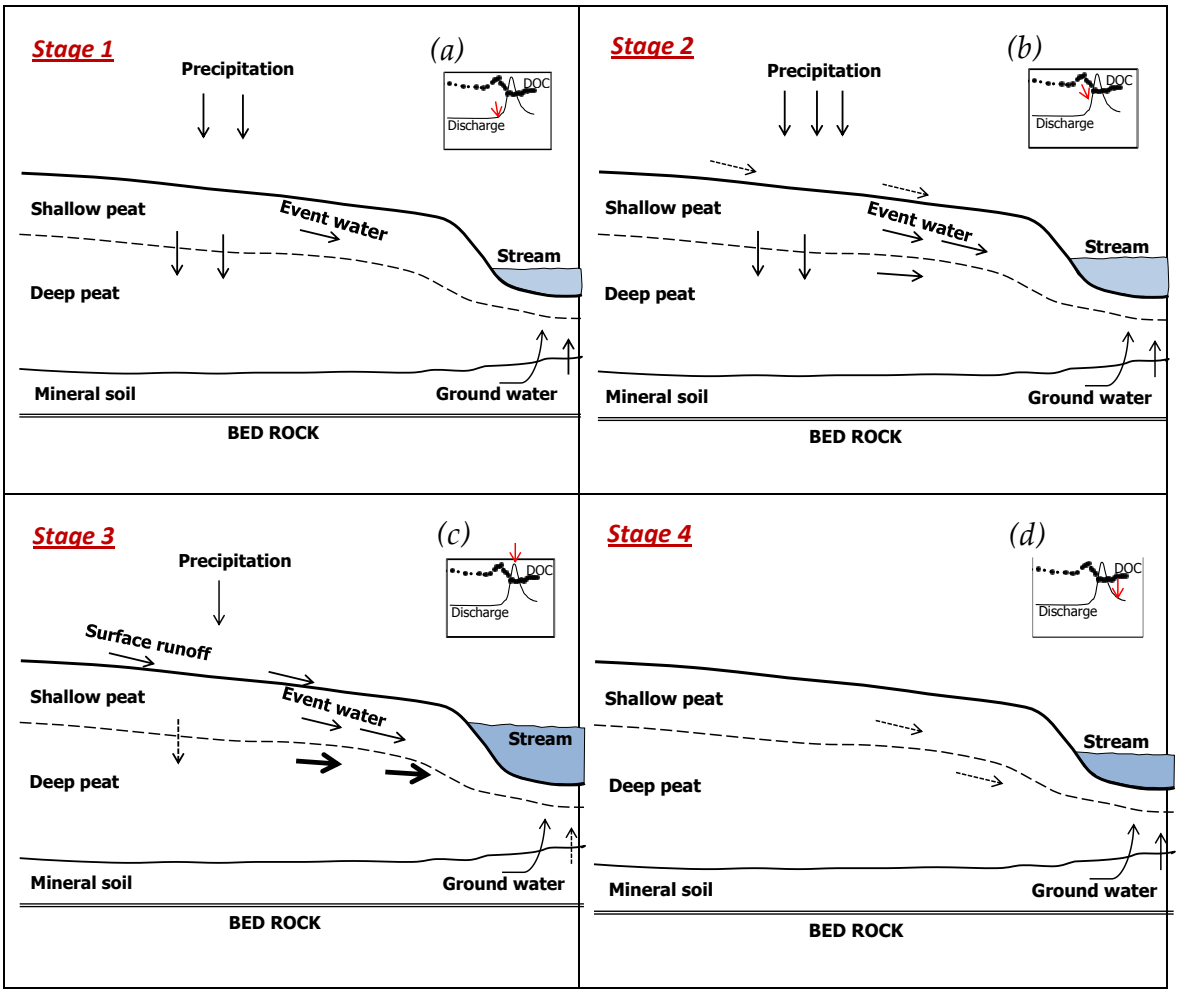


Figure 7.20: Conceptual model for the evolution of DOC in the intact site, represented in four stages of varying hydrograph.

Stage 4: *Receding limb of the hydrograph (Figure 7.20d).* Waters from deeper sources and/or groundwater sources are dominantly input to the stream

characterized by higher concentrations of weathering derived base cations like, Ca, Mg, Na and K.

Forested and Felled sites

Stage 1: *Early stages of the rising limb of hydrograph (Figure 7.21a).* As the rainwater infiltrates watertable tend to rise, and pre-event water in the riparian zone tend to form a wedge near the stream channel.

Stage 2: *Rising limb of the hydrograph (Figure 7.21b).* As the event progresses, laterally moving event water displaces the pre-event water (with relatively long residence times). Stream chemistry at this stage is dominated by the signature from the pre-event waters (rich in Fe, Al, Ca, and Mg).

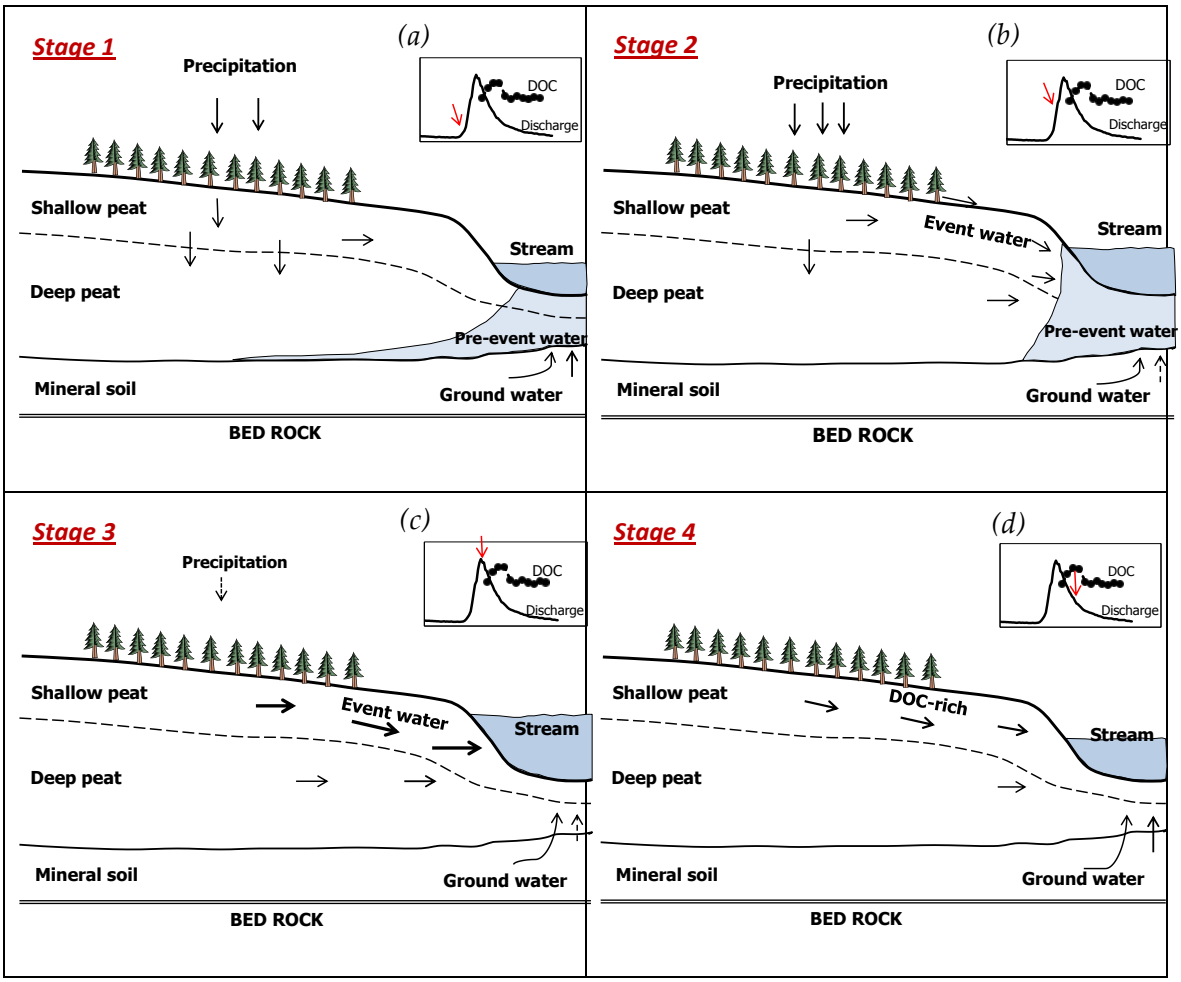


Figure 7.21: Conceptual model for the evolution of DOC in the forested and felled sites (felled tree litter replace the trees), represented in four stages of varying hydrograph.

Stage 3: *Peak discharge (Figure 7.21c)*. Rapid flow of eventwater through macropores (rootzones, pipes etc) with minimal interaction with available DOC-rich sources dominate the stream discharge. Streamwater is characterized by low DOC concentrations and reduced concentrations of Fe, Al, Ca and Mg in this stage.

Stage 4: *Receding limb of the hydrograph (Figure 7.21d)*. Shallow subsurface event water with relatively longer residence times and enriched in DOC tend to dominate the stream flow. DOC is flushed from the acrotelm with peak DOC concentrations occurring at this stage, followed by post-event water from deep soil or groundwater sources that dominate the later stages.

7.12. Conclusions

Main conclusions of this investigation in three different sub-catchments of River Dyke catchment are:

i) Higher DOC concentrations are generally associated with summer storm events.

ii) Streamwaters in the catchment are dominated by DOC, while POC accounts for about 6 - 10% of the total organic carbon exports.

iii) Evidence from E_4/E_6 ratio suggests that majority of DOC exported during storm events is relatively younger and sourced from near-surface layers (< 50cm depth) of peat.

iv) A similar DOC export mechanism is evident for the forested and felled, which differ to that for the intact site.

v) The DOC analysis results are consistent with the three end-member system proposed by Worrall *et al.* (2002). Defined by the pre-event water marked by low DOC concentrations and event water (two types) characterised by – event water rich in DOC in the initial

stages of hydrograph gives way to new water depleted in DOC during peak and later stages of hydrograph, vice-versa is true for the forested and felled sites. However, hydrologically each sub-catchment has two end-members: event water, pre-event water (or old water).

Chapter 8
ORGANIC CARBON LOADS

This chapter presents the analysis and estimates of fluvial organic carbon loads from the Dyke catchment, and concludes with a discussion on the variability of loads across the catchment.

8.1 Introduction

Although peatlands are the biggest global stores of organic carbon, studies have suggested that changes in climate and landuse may drive peatlands to be both sinks and sources of carbon (Waddington and Roulet, 1996; Cannell *et al.*, 1999; Worrall *et al.*, 2003; Smith *et al.*, 2004). The majority of such studies only account for gaseous emissions (*eg.* CO_2 and, CH_4), and exclude the fluvial fluxes of carbon from peatlands. Although relatively small compared to other terrestrial carbon fluxes, fluvial exports of carbon provide a key linkage between the soil and ocean C pools (Dawson *et al.*, 2004), are an important source of energy to aquatic ecosystems, and play a major role in controlling the physical, chemical and biological processes in waters (Hader *et al.*, 1998; Hruska *et al.*, 1999; Limpens *et al.*, 2008). The fluvial flux of carbon from a peatland occurs in the form of dissolved organic carbon (DOC), particulate organic carbon (POC) and dissolved inorganic carbon (DIC). In upland acidic peat systems, DOC and POC derived from terrestrial sources are the important components of carbon in stream water (Grieve, 1991; Hope *et al.*, 1997). Recently, evidence of large increases in DOC concentrations of river water has been published (Freeman *et al.*, 2001; Worrall and Burt, 2004; Worrall *et al.*, 2007), associated with increasing temperatures, changes in landuse, pH and discharge (Grieve, 1990; Freeman *et al.*, 2001; Tranvik and Jansson, 2002; Worrall *et al.*, 2006, 2007). Therefore, as there are three different landuse areas in this study, the impact of changes in landuse and stream discharge on DOC export are of primary interest. DOC and

discharge data from the three different landuse sites *(Figure 8.1)* in the Dyke catchment are used to assess the annual DOC fluxes from each sub-catchment, and from the whole catchment. In addition to comparing the spatial variability in concentrations and fluxes of DOC at the three sites, and at a downstream site in the Dyke catchment, DOC loads are calculated from individual sub-catchments to identify major sources of DOC within the catchment, and are integrated to produce a catchment-scale annual budget of DOC export.

8.2 Seasonal controls on DOC

The most important factor linked to DOC dynamics in streams is discharge, and it has been widely accepted that the majority of the total annual export of DOC from catchments is transported during high-flow events (Hinton *et al.*, 1997; Schiff *et al.*, 1997; Clark *et al.*, 2007; Koehler *et al.*, 2009). However, in many upland catchments, seasonality is observed to influence DOC concentrations (Proctor, 1994; Koehler *et al.*, 2009; Dawson *et al.*, 2011) in addition to the variability that is linked directly to discharge alone. In general, the DOC response to discharge varies between seasons, with summer and autumn concentrations being higher than spring concentrations under similar discharge conditions (Dawson *et al.*, 2008, 2011; Koehler *et al.*, 2009). Possible causes of such a seasonality in DOC could be variable production rates due to changes in microbial activity associated with varying temperatures, and antecedent soil-moisture conditions in the catchment (Freeman *et al.*, 2001; Ågren *et al.*, 2008; Dawson *et al.*, 2011). To examine the seasonal variations in the DOC concentrations, instantaneous and continuous discharge data were analysed by season (Wilby, 2001; Tank *et al.*, 2005), and each season includes three months of data: spring (March-May), summer (June-August), autumn (September-November) and winter (December – February).

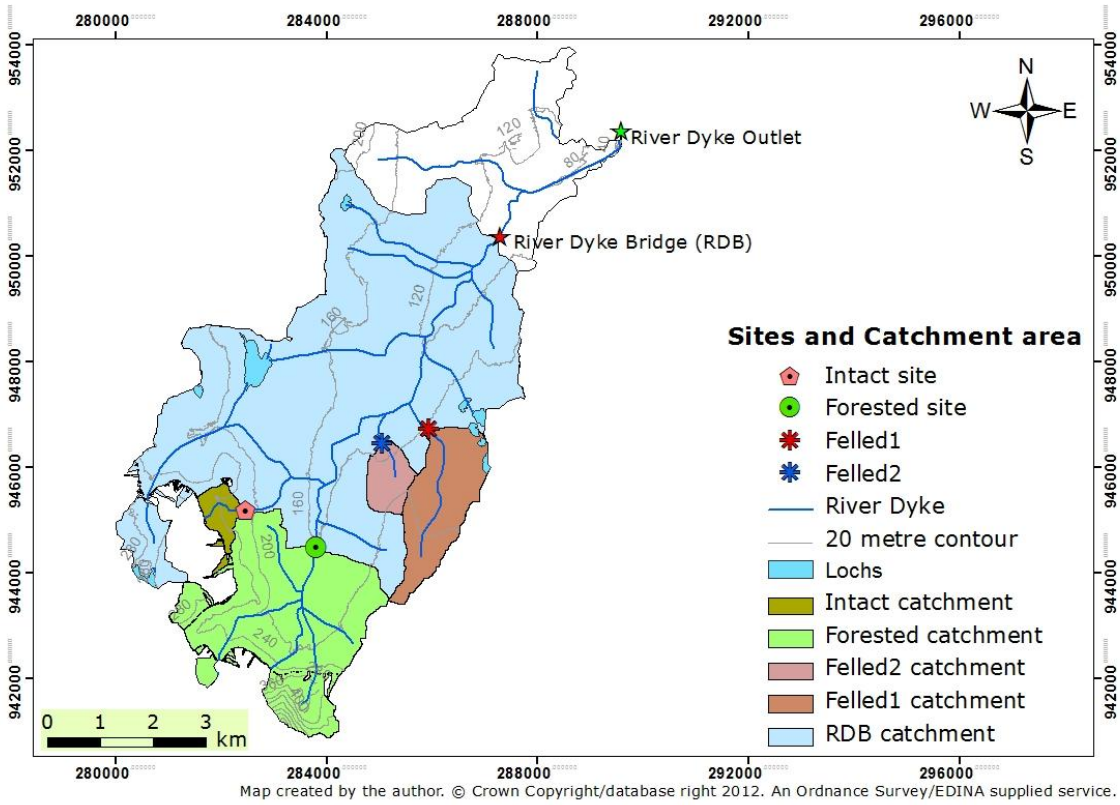


Figure 8.1: Map showing monitoring sites in the Dyke catchment (53.9 km²). Upstream catchment area for sites: RDB - 44.4 km², felled1 - 3.8 km², felled2 - 0.95 km², forested - 9 km², and intact - 0.69 km².

8.2.1. DOC, discharge and temperature

As seasonal variations in DOC concentrations are evident from the data, an attempt was made to re-model discharge-DOC relationships (see Chapter 7) by including temperature as an additional variable. The air temperature data provided by CEH (measured in 15-minute intervals at Allt Bhreun Bhaid - NC84744 46442) showed no significant relationship with DOC concentrations, hence air temperature data was not used for further analysis. However, correlations are observed between DOC from individual sites and stream water temperature (measured at 30-minute interval alongside stage level, at the forested site). The relationships between DOC - discharge and temperature (^{0}C) are provided in *Table 8.1*. From the table, significant improvements in the regression models are evident for all sites when compared to previous DOC-

discharge regressions *(Table 7.5)*. Results also show considerable increase in the coefficient of determination (r^2) values, and a marked reduction in standard error of estimates for all sites, particularly at the felled site *(Table 7.5 & Table 8.1)*. This suggests that biological activity related to temperature during different seasons of the year could be a control on DOC transport, in addition to flushing related to discharge (Andrews *et al.*, 2011).

Table 8.1: Seasonal variation in the relationship between discharge (Q) in $m^3\ s^{-1}\ km^{-2}$, temperature (^0C), and DOC concentrations in mg C L^{-1}.

Season	Site	Relationship	R^2 (%)	N	SE
SUMMER	*Intact*	DOC = 47.2 + 7.2 log Q - 11.3 log T	55.7 [a]	125	3.4
	Forested	DOC = 122 + 13.3 log Q - 69 log T	73.1 [a]	100	4.4
	Felled1	DOC = 80.8 + 14.4 log Q - 16.5 log T	54.5 [a]	52	6.4
	Felled2	DOC = 277 - 0.5 log Q - 200.6 log T	70.1 [a]	81	5.3
AUTUMN & WINTER	*Intact*	Log(DOC) = 0.1 - 0.01 log Q +1 log T	86.4 [a]	23	0.1
	Forested	DOC = 1.8 + 6.8 log Q + 25.4 log T	83.0 [a]	23	3.7
	Felled	DOC = - 12.6 - 20 log Q + 7.0 log T	90.2 [a]	23	6.6
SPRING	*Intact*	DOC = 10 +0.02 log Q + 3.54 log T	27.3 [a]	47	1.0
	Forested	DOC = 18.4 + 1.6 log Q - 1.5 log T	09.0 [b]	65	1.8
	Felled	DOC = 52 + 2.0 log Q - 16.6 log T	56.1 [a]	45	2.4

[a] significance at < 0.001 ; [b] significance at < 0.05, SE – standard error

These relationships can be used to develop a time series of DOC concentrations (Hobbie and Likens, 1973; Edwards *et al.*, 1984) in order to estimate the annual DOC loads from each sub-catchment and from the entire Dyke catchment. DOC concentrations were estimated for each discharge and temperature value with a 30-minute interval for the entire study period. The predicted DOC concentrations were compared against corresponding measured DOC values in stream water samples *(Figure 8.2)*. The correlation yielded a

positive linear trend with a Pearson correlation coefficient of 0.97 and a R^2 value of 93.2%, both significant at $p < 0.001$. The estimated time-series of DOC concentrations have been subsequently used to calculate DOC loads for each site as detailed in the following section.

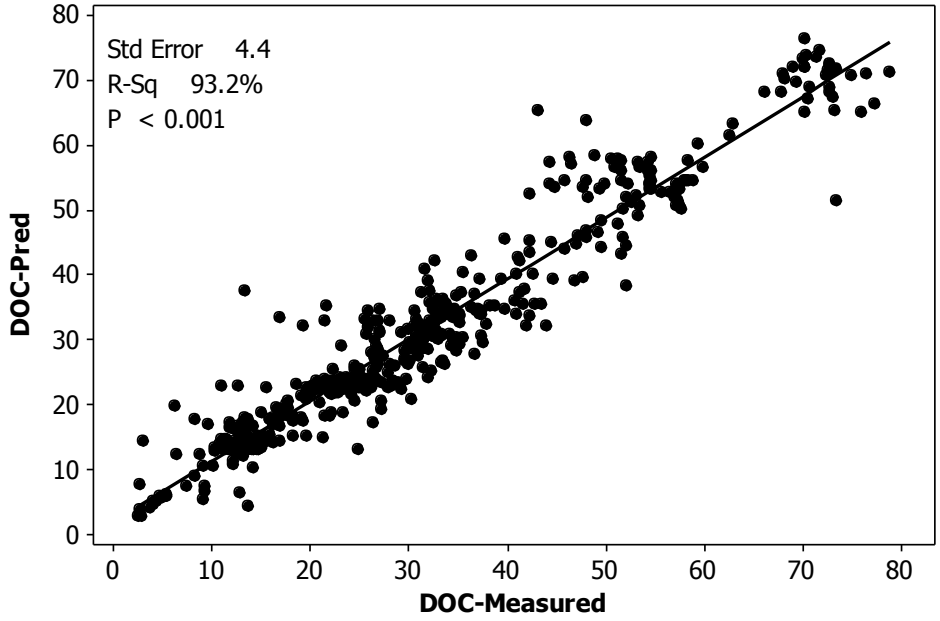


Figure 8.2: Correlation between measured and predicted DOC (from its relationship with discharge and temperature) for the sampling period (2009 - 2011); data from all sites combined. DOC displayed in mg C L^{-1}.

8.3 DOC Load estimation

When continuous discharge and DOC concentration data are available, then reliable load estimates can be calculated (Littlewood, 1992). Since discharge data are spaced regularly in time (30 minute intervals), the relationships in Table 8.1 can be used to calculate DOC loads with acceptable error as the sum of the product of flow and concentration, scaled by the time interval (Littlewood, 1992) in the following manner:

$$Load = K.\Delta t.\sum(C_i\ Q_i)$$

(Eq 8.1)

where, K is a conversion factor to account for the units, Δt is the data time interval, C_i is the DOC concentration of i^{th} sample, and Q_i is the corresponding discharge.

Worked example:

For example, the sum of the product of concentration (C) and discharge (Q) for 'i' number of samples ($\sum C_i \times Q_i$) is 400 mg C $L^{-1} \times m^3\ s^{-1}$, and sampling time interval, Δt = 0.5 hour (30 minutes), conversion factor (for units) 'K' can be calculated as follows:

Units of $\Delta t \times C_i \times Q_i$ = hr × mg C $L^{-1} \times m^3\ s^{-1}$

= 3600s × mg C L^{-1} × 1000 L s^{-1} (since, 1hr = 3600s & $1m^3$=1000L)

= 3600 × mg C × 1000

= 3.6 kg C

=> conversion factor, K = 3.6

Therefore, DOC load = $K.\ \Delta t.\ \sum C_i Q_i$

= 3.6 × 0.5 × 400 kg C

= 720 kg C

For this study, *Eq 8.1* was used to calculate the annual dissolved organic carbon fluxes for all sites. Since the loads are calculated using continuous discharge and event DOC concentration data, the results are anticipated to be close to the true load (Littlewood, 1992), with an error of < 1%. The resulting DOC loads and uncertainty in the estimates for each site were expressed both as the total amount of organic carbon exported in kg C $year^{-1}$ and as the export per hectare of catchment upstream of the monitoring point in kg C ha^{-1} $year^{-1}$ *(Table*

8.2). The catchment areas were derived from the 1:10,000 DTM (downloaded from Ordnance Survey/EDINA).

Since the flow and concentration data used in this study are of high frequency, the uncertainty due to load estimation method are likely to be small (Littlewood, 1992). Even so, since the calculated annual loads are only estimates of the true load, it is important to quantify the standard errors and 95% confidence limits for the load estimates. However, much of the error in the flux estimates is likely to be introduced due to the uncertainty in the DOC - discharge model used to estimate continuous DOC concentrations. Therefore, the uncertainties in the estimates (95% confidence limits) are approximated by adding up the errors from the DOC - discharge regressions and the errors from flux estimation.

8.3.1. Annual DOC fluxes for the year 2010

For the year 2010, sites received a rainfall total of 1050 mm and total discharge for this year for the intact, forested and felled sites is 4504×10^3, 17625×10^3 and 1859×10^3 cubic meters, respectively. Mean DOC concentrations for the sites for year 2010 are 13.7, 14.6 and 36.6 mg C L^{-1} for the intact, forested and felled sites, respectively *(Table 8.2)*. Annual DOC loads and yields for sites and uncertainties are listed in *Table 8.2*. Seasonal variability in DOC loads for each site is evident. At the intact site, highest DOC loads ($28.8 \pm 2.8 \times 10^3$ kg C) occur during summer months and the lowest ($4.32 \pm 0.14 \times 10^3$ kg C) during the winter months *(Figure 8.3)*. On the other hand in the forested site, highest DOC loads ($144.5 \pm 26.6 \times 10^3$ kg C) seem to occur in winter months and lowest loads ($65 \pm 8.6 \times 10^3$ kg C) occur during summer. In the felled site, the majority of DOC ($20.3 \pm 3.03 \times 10^3$ kg C) is exported during autumn with the lowest ($12.7 \pm 1.1 \times 10^3$ kg C) during summer months.

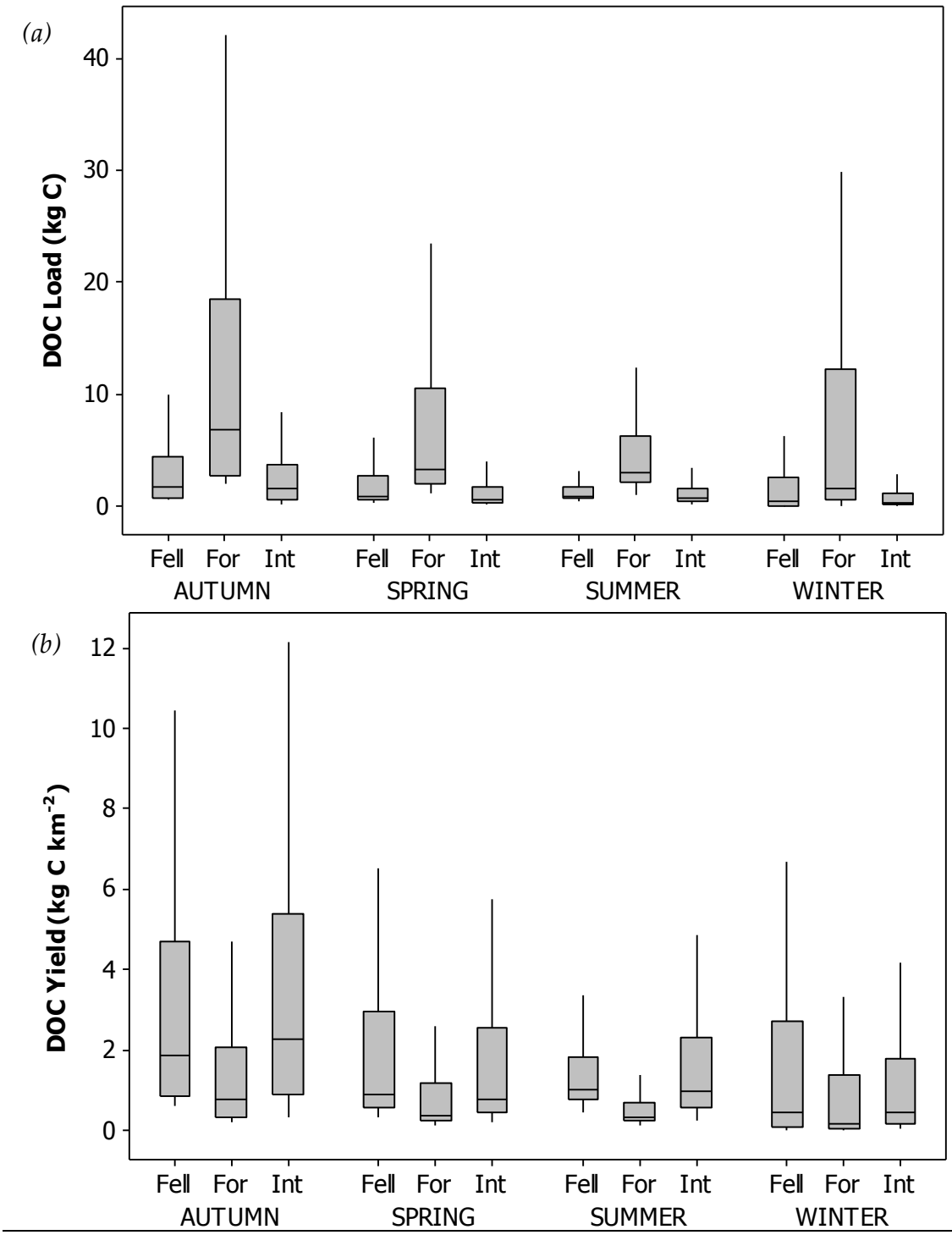


Figure 8.3: Boxplots illustrating seasonal variability in (a) DOC loads (kg C), and (b) DOC yields (kg C km^{-2}) for the year 2010. Sites: Fell-Felled, For-Forested, and Int-Intact.

Table 8.2: Seasonal fluxes and yields (at 95% confidence limits), and mean DOC concentrations for 2010. Uncertainties (95% confidence levels) in the estimates enclosed in brackets. Catchment area for sites: Intact - 0.7 km², Forested - 9 km², Felled - 0.95 km², RDB – River Dyke bridge (44.4 km²), River Dyke – 53.9 km² and River Halladale - 267 km² .

Season	Site	Mean DOC (mg C L^{-1})	Total discharge (10^3 m^3)	DOC Load (10^3 kg C)	DOC Yield (kg C ha^{-1})
SUMMER (June-Aug)	*Intact*	24.5	824.9	28.8 (2.8)	415.9 (40.9)
	Forested	22.0	1940.4	64.95 (8.6)	72.2 (9.6)
	Felled	60.4	204.7	12.7 (1.1)	134.3 (11.5)
AUTUMN (Sept-Nov)	*Intact*	14.5	1281.4	20.7 (0.14)	298.4 (2.0)
	Forested	15.7	4344.5	84.3 (16.1)	93.7 (17.9)
	Felled	39.0	458.1	20.3 (3.03)	214.4 (32.0)
WINTER (Dec-Feb)	*Intact*	3.1	1417.7	4.32 (0.14)	62.3 (2.1)
	Forested	5.9	7137.4	144.5 (26.6)	160.7 (29.5)
	Felled	9.8	752.8	14.7 (5.0)	155.4 (52.5)
SPRING (Mar-May)	*Intact*	12.6	980.5	11.5 (1.0)	166.2 (14.2)
	Forested	14.7	4203.2	68.9 (7.6)	76.6 (8.5)
	Felled	36.5	443.3	18.6 (1.1)	196.0 (11.3)
TOTAL (1 year)	*Intact*	13.7	4504.3	65.34 (4.1)	942.9 (58.8)
	Forested	14.6	17625.4	362.6 (58.7)	403.3 (65.3)
	Felled	36.6	1858.7	66.4 (10.1)	700.1 (107.0)
	RDB	22.8	87037.4	2247.8 (289.7)	506.3 (65.24)
	River Dyke	23.6	105660.4	2811.3 (351.6)	521.6 (65.24)
	River Halladale	30.0	523400.7	17297.7 (1742.3)	647.9 (65.3)

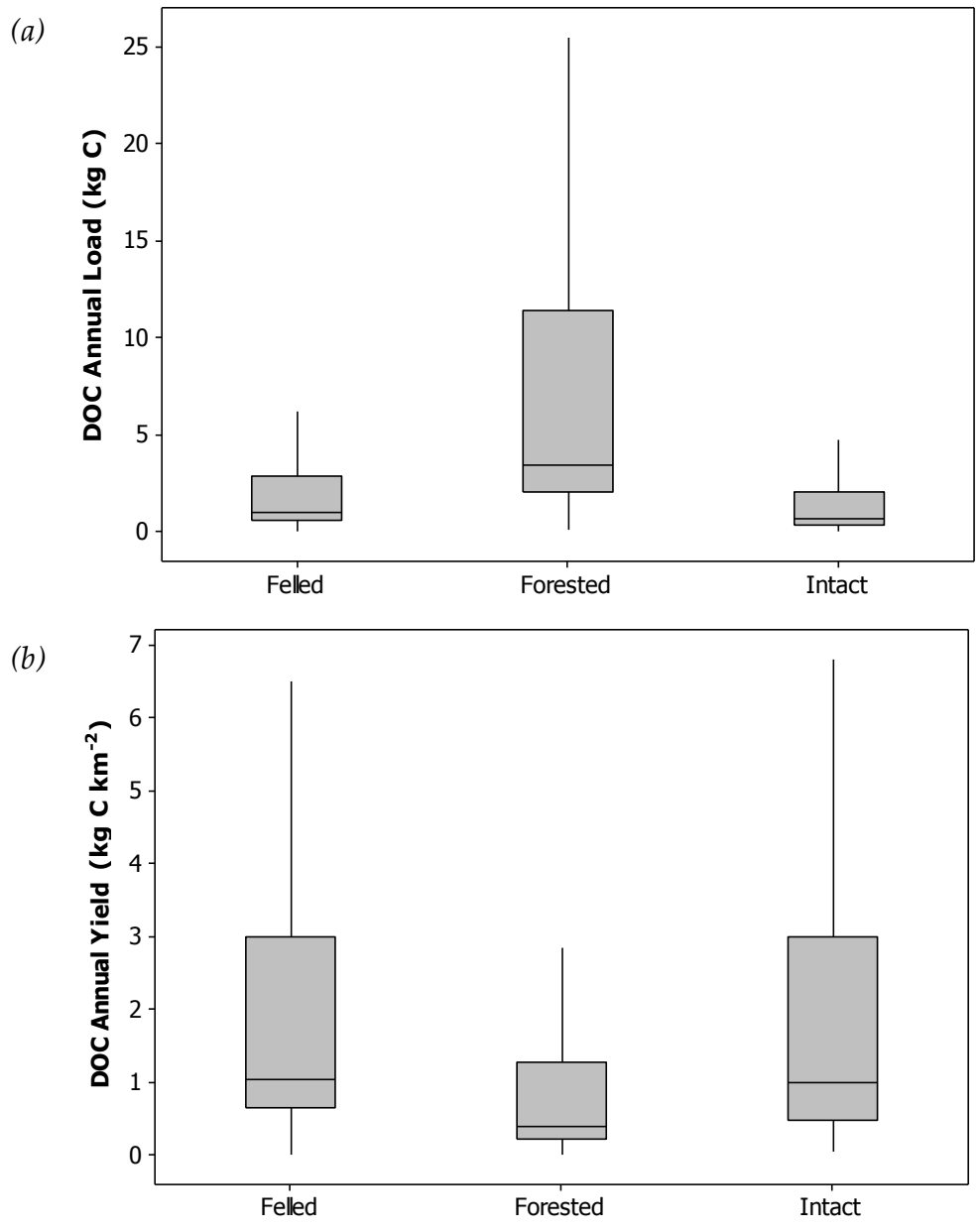


Figure 8.4: Boxplots illustrating (a) DOC annual loads (in kg C), and (b) annual yields (in kg C km^{-2}) from the sites for the year 2010.

DOC production in summer and spring months tends to be relatively high due to the rise in temperatures (Freeman *et al.*, 2001; Worrall *et al.*, 2008), and available DOC is flushed during late summer (intact site), autumn (felled site), and winter (forested) months. Total annual load from the forested site, with the larger catchment area *(Figure 8.1)*, is higher (362.6 ± 58.7 × 10^3 kg C year^{-1}) compared to the other sites, followed by the felled (66.4 ± 10.1 × 10^3 kg C year^{-1}) and intact (65.3 ± 4.1 × 10^3 kg C year^{-1}) sites *(Table 8.2 & Figure 8.4a)*. In

contrast, annual yields are highest in the intact site (942.9 ± 58.8 kg C ha^{-1} $year^{-1}$) followed by the felled (700.1 ± 107.0 kg C ha^{-1} $year^{-1}$) and forested (403.3 ± 65.3 kg C ha^{-1} $year^{-1}$) sites *(Figure 8.4b)*. The 95% confidence intervals for the DOC fluxes from sites are ± 5% for the intact, ± 16.2% for the forested and ± 15.3% for the felled sites.

The River Dyke bridge site (RDB), a downstream site on the River Dyke close to the confluence with the River Halladale, accounts for an upstream area of about 82.4% (44.4 km^2) of the total Dyke catchment area (53.9 km^2). Other than the gauging stations set up as part of this project, the River Dyke is ungauged. Discharge is estimated using the area-weighted discharge data from the forested site, and a time series of DOC concentrations is estimated using the continuous discharge and temperature data. At this site, mean DOC concentrations and total discharge for 2010 are estimated to be 22.8 ± 0.1 mg C L^{-1} and 87037 × 10^3 m^3, respectively; total annual DOC load and yields are 2248 ± 289.7 × 10^3 kg C $year^{-1}$ and 506.3 ± 65.2 kg C ha^{-1} $year^{-1}$, respectively *(Table 8.2)*.

The specific discharge (m^3 s^{-1} km^{-2}) from the forested site is also used to develop a time series of discharge for the entire Dyke catchment, which covers an area of ~ 53.9 km^2. A time series of DOC concentrations were computed using the relationship between DOC, discharge and water temperature from the RDB site (as this site is the closest to the outlet). For the Dyke catchment, the mean DOC concentrations and total discharge for the year 2010 are estimated to be 23.6 ± 0.1 mg C L^{-1} and 105660 × 10^3 m^3, respectively. The total annual DOC load and annual DOC yield for the entire catchment are 2811.3 ± 351.6 × 10^3 kg C $year^{-1}$ and 521.6 ± 65.2 kg C ha^{-1} $year^{-1}$, respectively *(Table 8.2)*. The 95% confidence intervals for DOC fluxes from the RDB site and the Dyke catchment are ± 12.9% and ± 12.5% respectively.

Subsequently, a time series of discharge and DOC concentrations were developed for the River Halladale, which covers an area of ~ 267 km^{-2}, by up scaling the data from the Dyke catchment. Although the uncertainty associated with such an up scaling is anticipated to be high, it has been attempted to provide approximate estimates of DOC loads from the Halladale catchment that can be compared with previously published results for the catchment. Thus, for the Halladale catchment, the mean DOC concentrations and total discharge for the year 2010 are estimated to be 30.0 ± 1.0 mg C L^{-1} and 523401 × 10^3 m^3, respectively. The total annual DOC load and annual DOC yield for the catchment are 17297.7 ± 1742.3 × 10^3 kg C $year^{-1}$ and 647.9 ± 65.3 kg C ha^{-1} $year^{-1}$, respectively *(Table 8.2)*.

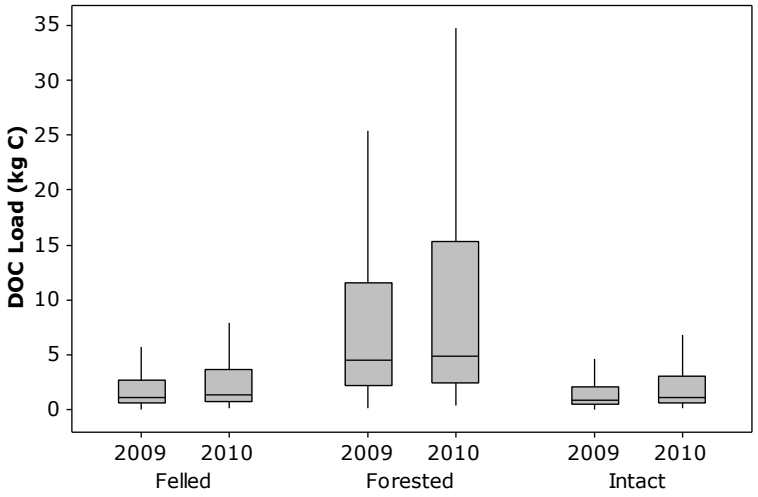
8.3.2. DOC loads comparison - 2009, 2010 and 2011

Data collection started in July 2009 and lasted until early April 2011 (see Chapter 4 for details on monitoring periods). Therefore, the results from 2009 and 2011 are compared against that of 2010 where the data are available for the entire year *(Table 8.3)*. That is, summer and autumn loads from 2009 are compared with that of 2010, and winter loads of 2011 are compared with that of 2010. Summer data include July and August as these months have data for 2009. Similarly, winter data for each year include December of the previous year as well as January and February of a given year. A comparison of seasonal annual loads, mean DOC and discharge for the sites are listed in *Table 8.3*.

During the second half (July-Dec) of 2009 and 2010, the total amount of rainfall received by the catchment was 805.4 and 679.2 mm, respectively. Total amount of rainfall received during summer and autumn months of 2009 and 2010 decreased by ~ 38% and 32%, respectively. During summer 2010, 85% increase in discharge in the intact site, and about 22% decrease in that of the forested and felled sites is evident, while a 7% increase during autumn 2010 in

the intact site, and about 30% increase in discharge for the same period in the forested and felled sites, are observed. A two-fold increase in summer DOC loads and an 11% increase in autumn loads are evident in the intact site during 2010 compared to that in 2009 *(Table 8.3)*. On the other hand, a 24% and a 37% decrease in the summer and autumn loads, respectively, occur at the forested site, and a 7%, and a 36% decrease in loads during the same period are evident at the felled site. When summer and autumn loads in 2009 are compared for the same period with that in 2010, DOC loads increased at the intact site by 51%, and decreased by 32% and 28% at the forested and felled sites, respectively.

(a)



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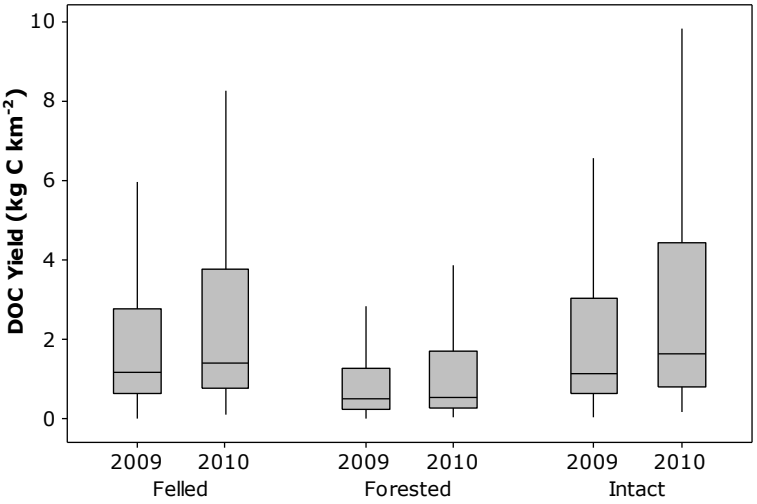

Figure 8.5: Comparison of (a) DOC loads (kg C) and (b) DOC yields (kg C km^{-2}) from sites between 2009 & 2010.

During winter months, total precipitation increased about two fold from 153 mm in 2009/10 to 330 mm in 2010/11, which resulted in a 27%, 36% and 36.3% increase in discharge in the intact, forested and felled sites respectively. Similar significant increases in DOC loads were observed at the intact (86%) forested (146%) and felled (92%) sites *(Table 8.3)*.

On comparison of DOC fluxes from the sites for the same period between 2009 and 2010, an increasing trend of DOC export is observed at the intact and forested sites, whereas a decreasing trend is evident for the felled site *(see Figure 8.5 & Table 8.4)*. Upward trends in the intact and forested site could be attributed to the increase in discharge, for example, 52% increase in discharge at the intact site increased the load by a similar amount (~ 54%), and a 5% increase in discharge at the forested site increased the DOC load by ~ 10.4%. In contrast, a 5% increase in discharge, is associated with an 11.3% decrease in the load at the felled site *(see Figure 8.5 & Table 8.4)*.

At the RDB site (close to the outlet of the Dyke catchment), total DOC load and yields for 2009 (July-Dec) are 1635.2 ± 172.1 × 10^3 kg C and 368.3 ± 38.8 kg C ha^{-1} respectively *(Figure 8.6 & Table 8.4)*. For the same period in 2010 at this site, DOC load and yield are estimated to be 1419.5 ± 178.2 × 10^3 kg C and 319.7 ± 40.1 kg C ha^{-1}, about 13% less from that of the previous year, and about 5% decrease in the discharge is observed *(Table 8.4)*.

For the entire Dyke catchment, total DOC load and yields for 2009 are 2027 ± 208.9 × 10^3 kg C and 376.1 ± 38.8 kg C ha^{-1} *(Figure 8.6 & Table 8.4)*. However, for the same period in 2010, DOC loads from the catchment are estimated to be 1767.1 ± 216.4 × 10^3 kg C and 327.9 ± 40.1 kg C ha^{-1}, decreased by 12.8% compared to that of the previous year *(Table 8.4)*.

Table 8.3: A comparison of seasonal DOC loads and yields, and mean DOC concentrations for 2009 and 2010. Uncertainties (95% confidence levels) in the estimates enclosed in brackets. Catchment area for sites: Intact - 0.7 km², Forested - 9 km², and Felled - 0.95km²

Season	Site	Year	Mean DOC (mg C L^{-1})	Total discharge (10^3 m^3)	DOC load (10^3 kg C)	DOC Yield (kg C ha^{-1})
SUMMER (June-Aug)	*Intact*	*2009*	24.1	430.6	13.8 (1.5)	198.9 (21.3)
		2010	25.8	797.4	28.2 (2.8)	407.0 (39.7)
	Forested	*2009*	21.4	2277.7	80.1 (10.1)	89.1 (11.3)
		2010	23.0	1761.8	61.2 (7.8)	68.1 (8.7)
	Felled	*2009*	37.4	240.1	12.3 (1.6)	130.2 (16.4)
		2010	58.7	185.8	11.5 (1.0)	121.2 (10.5)
AUTUMN (Sept-Nov)	*Intact*	*2009*	15.5	1201.0	18.6 (0.13)	268.5 (1.9)
		2010	14.5	1281.4	20.7 (0.14)	298.4 (2.0)
	Forested	*2009*	16.2	6086.9	134.0 (22.6)	149.0 (25.2)
		2010	15.7	4344.5	84.3 (16.1)	93.7 (17.9)
	Felled	*2009*	40.7	641.9	32.0 (4.3)	337.3 (44.9)
		2010	39.0	458.1	20.3 (3.0)	214.4 (32.0)
WINTER (Dec-Feb)	*Intact*	*2010*	4.7	952.0	2.9 (0.1)	41.5 (1.4)
		2011	5.2	1213.0	5.4 (0.1)	78.3 (1.8)
	Forested	*2010*	4.4	4430.0	53.1 (16.5)	59.1 (18.3)
		2011	7.1	6035.9	130.4 (22.5)	145.05 (25.0)
	Felled	*2010*	8.2	467.1	7.3 (3.1)	77.3 (32.6)
		2011	14.7	636.5	14.0 (4.2)	147.4 (44.4)
SPRING (Mar-May)	*Intact*	*2010*	12.6	980.5	11.5 (1.0)	166.2 (14.2)
	Forested	*2010*	14.7	4203.2	68.9 (7.6)	76.6 (8.5)
	Felled	*2010*	36.5	443.3	18.6 (1.1)	196.0 (11.3)

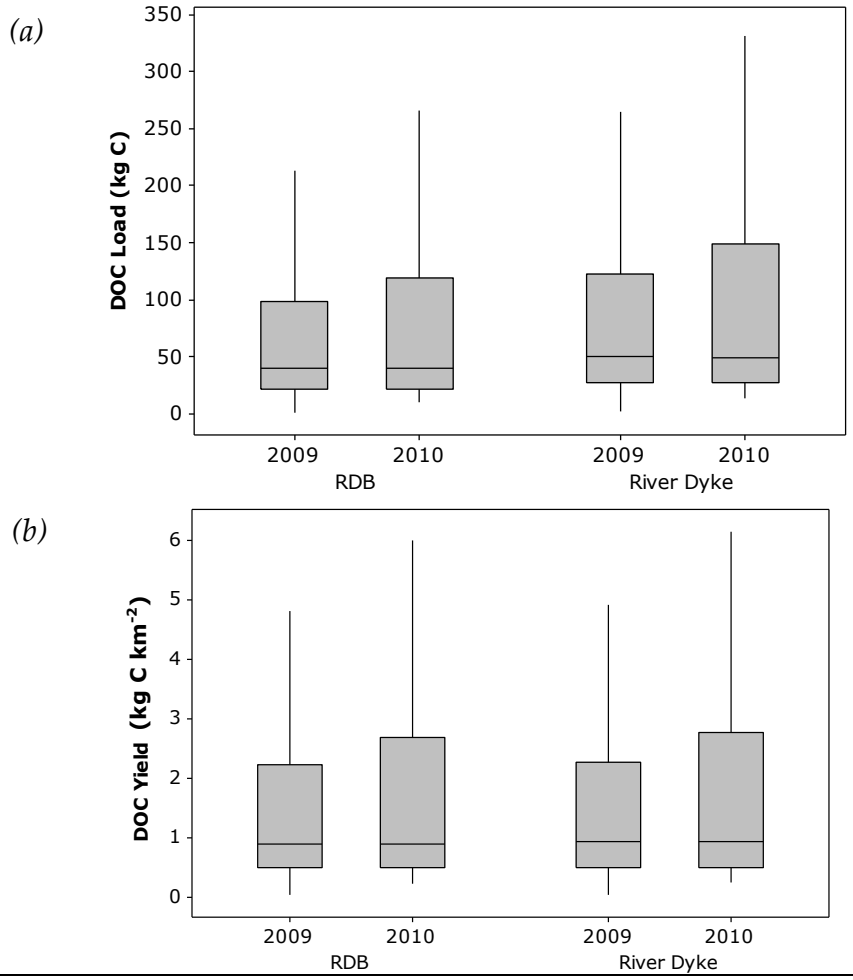

Figure 8.6: Comparison of (a) DOC loads (kg C), and (b) DOC yields (kg C km^{-2}) from River Dyke bridge site (RDB) and from the entire River Dyke catchment between 2009 & 2010.

8.4 Discussion

This study aimed to estimate the annual loads from the sub-catchments within the catchment, integrate them to calculate total loads leaving the entire catchment, and identify the likely effects of landuse change in the catchment. It has been hypothesized that the DOC concentrations leaving the disturbed (forested and felled) sites would be greater compared to that exported from the undisturbed bog.

Annual loads were calculated using a continuous flow and concentration data hence are expected to be very close to the true load with negligible error (Littlewood, 1992). Although, there may be a slight degree of overestimation as

the DOC concentrations were estimated from the continuous discharge data (Hobbie and Likens, 1973; Edwards *et al.*, 1984), and increase in discharge not always necessarily mean increase in DOC concentrations, especially when the storm events are closely spaced (Worrall *et al.*, 2002); this study shows that periods of high discharge are responsible for the majority of DOC export *(Figure 8.7)*. For example, stream discharge at the intact site exceeds ~ 0.4 m^3/s only 10% of the time, yet the proportion of DOC exported during that high flow period is ~57% *(Figure 8.7a)*. Similar results are observed at the forested site, where discharge exceeds ~ 2.2 m^3/s, only about 8% of time and is responsible for the top 60% of the DOC export during that 8% of time *(Figure 8.7b)*. At the felled site, where drain blocking prevents rapid runoff, 95% of DOC export occurs only during the upper 5% of the discharge values *(Figure 8.7c)*. These results are similar to studies in Canadian wetland (Hinton *et al.*, 1997), and in Cotton Hill Sike catchment in northern Pennines, UK (Clark *et al.*, 2007) where around 41-57% of DOC exported during the top 10% of high flows. Therefore, the uncertainty in the estimates, for a peat-dominated catchment like the one in this study, would be expected to be of a lower degree as, i) the majority of total annual DOC is found associated with high flows (Grieve, 1984; Hinton *et al.*, 1997; Schiff *et al.*, 1997; Clark *et al.*, 2007; Koehler *et al.*, 2009), and ii) the changes in water temperature were also taken into account (Andrews *et al.*, 2011). Hence, the annual load estimates presented in this study are likely to be closer to the 'true loads' as they include detailed quantification of DOC exports during high flows. Recent data from major world rivers show export of organic carbon to be highly correlated with annual river discharge, and is a function of factors like discharge and/or season in smaller catchments (Schlesinger and Melack, 1981; Hope *et al.*, 1994). Hence, in this study variability in DOC fluxes related to changes in stream discharge as well as seasonal effects are considered.

Table 8.4: A comparison of mean DOC concentrations, discharge, DOC loads and yields, between 2009, 2010 and the entire study period (2009-2011). Uncertainties (95% confidence levels) in the estimates enclosed in brackets. Upstream catchment area for sites: Intact - 0.7 km², Forested - 9 km², Felled - 0.95km², RDB – River Dyke bridge (44.4 km²), and River Dyke – 53.9 km².

Season	Site	Mean DOC (mgC L^{-1})	Total discharge (10^3 m^3)	Mean Load (kg C)	DOC Load (10^3 kg C)	DOC Yield (kg C ha^{-1})
2009[a]	*Intact*	16.5 (0.08)	1748.9 (0.4)	3.75 (0.1)	33.1 (1.6)	477.2 (23.2)
	Forested	15.8 (0.08)	8950.7 (2.9)	24.7 (1.0)	217.7 (34.8)	242.1 (38.7)
	Felled	34.1 (0.15)	943.9 (0.4)	5.1 (0.2)	45.2 (6.2)	476.6 (65.4)
	RDB	27.1 (0.1)	44200.4 (14.0)	185.6 (7.0)	1635.2 (172.1)	368.3 (38.8)
	River Dyke	27.9 (0.1)	53657.8 (17.1)	2027.0 (208.9)	376.1 (38.8)	376.1 (38.8)
2010[a]	*Intact*	16.5 (0.1)	2661.7 (0.7)	5.8 (0.3)	51.0 (2.9)	735.9 (42.2)
	Forested	16.8 (0.08)	9397.6 (2.7)	27.3 (1.2)	240.4 (36.1)	267.4 (40.2)
	Felled	41.3 (0.18)	991.1 (0.3)	4.55 (0.12)	40.1 (6.3)	422.8 (66.6)
	RDB	26.8 (0.1)	46407.1 (13.0)	161.2 (4.5)	1419.5 (178.2)	319.7 (40.1)
	River Dyke	27.6(0.1)	56336.6 (15.8)	200.6 (5.5)	1767.1 (216.4)	327.9 (40.1)
2009-2011[b]	*Intact*	13.7 (0.05)	7080.7 (0.5)	3.4 (0.08)	104.1 (5.93)	1502.4 (85.5)
	Forested	14.2 (0.04)	30285.4 (2.3)	20.5 (0.5)	630.7 (105.3)	701.4 (117.1)
	Felled	33.9 (0.1)	3193.9 (0.3)	3.9 (0.1)	121.2 (18.5)	1278.5 (0.2)
	RDB	23.7 (0.05)	149554.6 (11.9)	139.5 (2.5)	4290.7 (519.9)	966.4 (117.1)
	River Dyke	24.5 (0.05)	181553.8 (14.4)	173.9 (3.1)	5350.5 (631.1)	992.7 (117.1)

[a] period between July – December; [b] entire study period (July 2009 – April 2011)

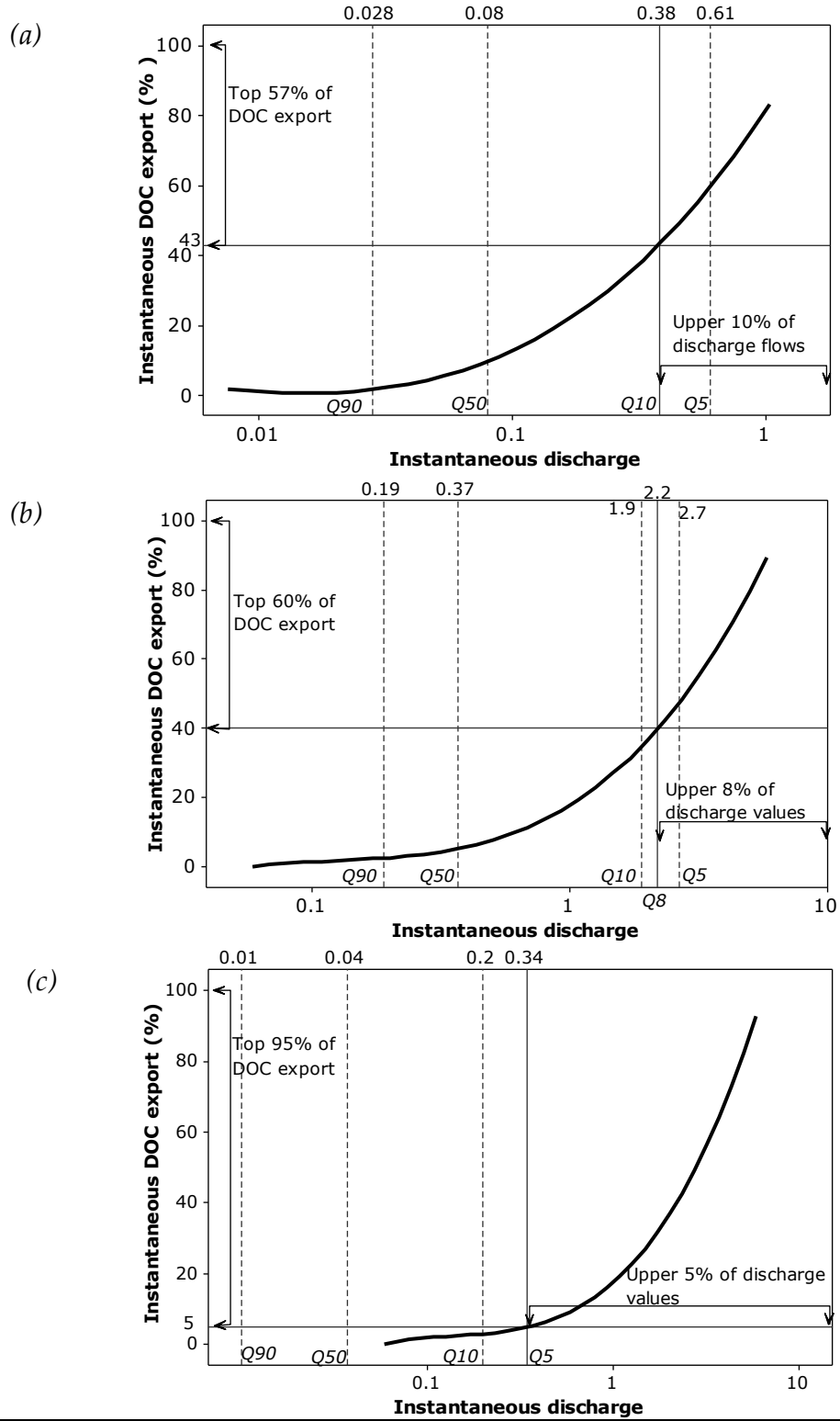

Figure 8.7: Percentage of DOC (measured) export as a function of percentage of time flow exceeded during the study period (2009-2011). (a) intact site - top 57% of DOC export is associated with the upper 10% of discharge values, (b) forested site - top 60% of DOC export with the upper 8% of discharge values, and (c) felled site - top 95% of DOC export with the upper 5% of discharge values. Instantaneous discharge is shown in log scale.

Total annual DOC concentrations leaving the catchment in the year 2010 are highest for the forested site (363×10^3 kg C year^{-1}) and lowest for the intact site (65×10^3 kg C year^{-1}). However, total annual DOC yields for sites ranged from 403 to 943 kg C ha^{-1} year^{-1}, the highest being from the intact site and lowest from the forested site. In general, highest fluxes are associated with late summer and autumn, suggesting flushing of DOC produced during dry summer months, while low winter fluxes are probably due to low production of DOC coupled with dilution by precipitation inputs. Spring fluxes appear to be intermediate between these two extremes. Nearly, 80% of the annual DOC loads of the Dyke catchment (for 2010) comes from the River Dyke bridge site, of all three main sites, the forested site is the biggest contributor with a ~ 13% load contribution, while about 2.4 % and 2.3 % comes from the felled and intact sites, respectively.

Changes in Annual DOC Fluxes

When the DOC loads for 2009 and 2010 are compared, an overall 12.8% decrease is evident for the Dyke catchment. While a decrease of 11.3% is suggested for the felled site, about a similar amount (10.4%) of increase in DOC fluxes is seen at the forested site. In contrast, the intact site exports nearly 54% more of its DOC in 2010 compared to that in the previous year. In a similar study in the Trout Beck catchment, Worrall *et al.* (2007) have predicted a 3% increase in DOC loss per annum from a pristine catchment which has been ascribed to changing climatic conditions. The changes in annual DOC loads are associated with a decrease in mean air (1.4^0C) and water (0.6^0C) temperatures, and an increase in discharge (5%-disturbed sites and 52%-undisturbed site) which generally suggest reduced DOC production and/or dilution of available DOC due to increased discharges.

Winter fluxes during 2009/10 and 2010/11 *(see Figure 8.3 & Table 8.2)* suggest increases in DOC fluxes from intact (86%), forested (146%) and felled

(92%) sites, as a result of increase in precipitation (two-fold), discharge (24-36%), water temperature (by 1.1^{0}C) and air temperature (by 1.2^{0}C). Similarly, an overall increase of ~90% in DOC fluxes leaving the Dyke catchment is evident for the same period, however, this increase is relatively small in magnitude compared to the overall decrease in annual loads between 2009 and 2010.

Landuse effects on DOC fluxes

In contrast to the hypothesis that disturbed sites lose more DOC compared to that of undisturbed sites, the intact site seems to release relatively more DOC than the other two sites. For example, on comparing summer and autumn months of 2009 and 2010, the intact site witnessed an increase in DOC fluxes of as much as 50%, while they decreased by about 30% in both the forested and felled sites.

Although the amount of rainfall received by the sites is the same as they are very closely spaced to each other, total discharge from the intact site increased by 27% while it decreased by a similar amount at both the forested and felled sites, resulting in the different changes in the DOC fluxes. A decrease in annual discharge in the forested site could probably be due to the reduction in water yield as a result of interception of precipitation and evapotranspiration losses (Calder and Newson, 1979; Neal *et al.*, 1986; Farley *et al.*, 2005). Compared to the other two sites, although maximum DOC fluxes leave this catchment, DOC lost per unit area is relatively low. In the felled site, the observed drop in discharge is perhaps due to the retention of water by ditch-blocking techniques, which reduce the flashy nature of this site and encourage vertical movement of water reducing the runoff (Holden *et al.*, 2004; Gibson *et al.*, 2009). Mean DOC concentrations from this site are consistently two times greater than that from the other sites; yet total annual DOC fluxes per unit area from this site are lower than that of the intact site. Therefore, the effects of tree felling to waste after 4-5

years do not seem to be significant in terms of DOC exports, although the installation of drain blocks may be successfully retarding carbon losses.

In contrast, depending on the antecedent soil-moisture conditions, the intact site appears to release the majority of the precipitation inputs as stream runoff (Anderson *et al.*, 2000). Hence, water yield coupled with availability of removable DOC appear to be principal controlling factors on DOC exports from the intact site.

Annual DOC fluxes from the Dyke catchment

Total annual DOC fluxes estimated for the Dyke catchment (for 2010) is 521.6 ± 65.2 kg C ha^{-1} $year^{-1}$ and for the River Halladale is 647.9 ± 65.3 kg C ha^{-1} $year^{-1}$, whereas for the year 1993, annual fluxes from the River Halladale catchment was estimated to be 103.4 ± 25.2 kg C ha^{-1} $year^{-1}$ by Hope *et al.* (1997b). Given the Dyke catchment accounts for about 20% of the Halladale catchment area, estimates in this study suggest that the previous estimates reported by Hope *et al.* (1997b) were significantly underestimated (acknowledged by the authors) as they did not account for DOC concentrations at peak discharges. Nevertheless, annual DOC loads from the Halladale catchment may have increased over 19 years, given the changes in climate and landuse, yet there seems to be a large difference (~ fivefold) compared to the loads calculated in this study.

Given the flashy nature of flow in peat systems, instantaneous flow and concentration measurements recorded at weekly or fortnightly intervals could lead to a greater degree of underestimation of annual fluxes (Hope *et al.*, 1997). Hence, the use of regular but infrequent sample data to calculate annual loads has been criticized (Walling and Webb, 1985). In this study, calculated loads are based on estimated concentrations from continuous discharge and water temperature data, and DOC concentrations measured during conditions such as: i) storm events in summer, spring and autumn months, ii) low flows in

summer, spring and winter months, iii) in between flood events, and iv) include different land-uses in the catchment when calculating the total annual loads. However, the loads presented in this study might be slightly overestimated, since they are computed from discharge values, and include uncertainties related to the method adopted for discharge measurements (Appendix II).

Total Organic Carbon (TOC)

In this study, particulate organic carbon (POC) concentrations do not show significant correlation with discharge and/or temperature, (discussed in Chapter 7) which limit the development of a reliable continuous POC record. Therefore, annual POC loads were calculated as a percentage of the DOC based on the proportions of POC relative to DOC in the measured samples, however uncertainty in such an approach is anticipated to be high. Annual loads of POC and total organic carbon (DOC + POC) and the uncertainty in the estimates are listed in *Table 8.5*.

Exports of POC showed the same trends as DOC in all three sites, although lower in magnitude with an estimated annual POC yield of 81.7 ± 17.6 kg C ha^{-1} $year^{-1}$ from the intact site, 27.4 ± 11.4 kg C ha^{-1} $year^{-1}$ and 34.9 ± 15.6 kg C ha^{-1} $year^{-1}$ from the forested and felled site, respectively. Similarly, annual POC yields of 34.5 ± 19.57 kg C ha^{-1} $year^{-1}$ and 35.5 ± 19.6 kg C ha^{-1} $year^{-1}$ are estimated for the downstream site (RDB) and for the entire Dyke catchment, respectively *(Table 8.5)*. Similar to the DOC loads, total POC fluxes from the forested site are higher due to its larger catchment area; in contrast, annual flux per unit area is lower than the intact site. The intact site seems to export more POC per unit area than the other sites, while loads from the felled site are estimated to be the lowest. Export of POC indicates the degree of disturbance and rates of peat erosion in the catchments (Holden *et al.*, 2004). In the intact site, the highest POC exports, during storm events in particular, probably

suggest high rates of peat erosion. Surprisingly, POC loads are relatively low from the felled-to-waste site, despite the presence of huge amounts of felled tree litter. This could be due to the ditch-blocking measures (as a part restoration) in this site, which curbs the flashy runoff and reduces the release of POC (Holden and Burt, 2002; Holden *et al.*, 2004).

Table 8.5: Annual organic carbon (OC) fluxes (at 95% confidence limits) and mean concentrations from the sites for 2010. Uncertainties in the estimates enclosed in brackets. Upstream catchment area for sites : Intact - 0.7 km², Forested - 9 km², Felled - 0.95 km², River Dyke Bridge (RDB) - 44.4 km² and River Dyke – 53.9 km².

Season	Site	Mean (mgC L^{-1})	Annual OC load (10^3 kg C $year^{-1}$)	Annual OC yield (kg C ha^{-1} $year^{-1}$)
DOC	*Intact*	13.7 (0.05)	65.34 (4.1)	942.9 (58.8)
	Forested	14.6 (0.04)	362.6 (58.7)	403.3 (65.3)
	Felled	36.6 (0.1)	66.4 (10.1)	700.1 (107.0)
	RDB	22.8 (0.05)	2247.8 (289.7)	506.3 (65.24)
	River Dyke	23.6 (0.05)	2811.3 (351.6)	521.6 (65.24)
POC	*Intact*	1.95 (0.16)	5.66 (1.23)	81.7 (17.6)
	Forested	1.5 (0.12)	24.6 (10.2)	27.4 (11.4)
	Felled	2.2 (0.15)	3.3 (1.5)	34.9 (15.6)
	RDB	1.88 (0.43)	153.1 (25.6)	34.5 (19.57)
	River Dyke	1.88 (0.86)	191.4 (25.8)	35.5 (19.6)
TOC	*Intact*	15.6 (0.21)	71.0 (5.33)	1024.6 (76.4)
	Forested	16.1 (0.16)	387.2 (68.9)	430.7 (76.7)
	Felled	38.8 (0.25)	69.7 (11.6)	735.0 (122.6)
	RDB	24.7 (0.5)	2400.9 (315.3)	540.8 (84.8)
	River Dyke	25.5 (0.9)	3002.7 (377.4)	557.12 (84.8)

Total organic carbon is computed as a summation of DOC and POC loads *(Table 8.5)*. POC concentrations ranged between 4 - 8% of total organic carbon exports, a similar range for POC was reported by Dawson *et al.* (2004). In the Dyke catchment, organic carbon is dominated by DOC (>90%), which is not surprising as in wetland catchments the majority of organic carbon is exported as DOC (Hope *et al.*, 1994). Total annual organic carbon fluxes from the Dyke catchment are 3002.7 ± 377.4 × 10^3 kg C ha^{-1} $year^{-1}$, with the majority loads coming from the forested site *(Table 8.5)*. However, the intact site is the biggest contributor (1025 ± 76.4 kg C ha^{-1} $year^{-1}$) of annual organic carbon yield to the catchment compared to the other two sites *(Table 8.5)*.

These results suggest that the disturbance caused by tree felling is not significantly impacting on the organic carbon loads over the study period, and possibly the blocking of drains in this site has successfully decreased the export of organic carbon (Gibson *et al.*, 2009). The forested site, which was drained prior to tree planting, also does not demonstrate a substantial loss of organic carbon. In contrast, the intact site indicates a greater loss of organic carbon (~50%) due to changes in precipitation, discharge and temperatures potentially caused by higher rates of peat erosion, although this has not been quantified in this study.

8.5 Conclusions

This study has shown that,

1. The results show that of the three sites studied, the majority of annual TOC/DOC export (in flux of DOC per unit area of catchment) comes from the intact site (~ 943 kg C ha^{-1} $year^{-1}$).
2. In addition, annual exports of DOC per unit area from the disturbed sites are lower and are mainly dependent on discharge.

3. DOC export from the sub-catchments studies seems to be a function of water yield. Hence, lower water yield of forested and felled sites during the study period resulted in lower annual DOC exports from these sites.
4. TOC loads from the Dyke catchment are a function of climate change in terms of discharge, precipitation inputs, temperature (seasonality) and water yield, rather than landuse change in the catchment.

Chapter 9
SUMMARY AND CONCLUSIONS

Peatlands are the biggest terrestrial stores of carbon and a principal source of organic carbon to fluvial environments. They are often considered as net carbon sinks, however continued disturbance of these C stores through landuse or climate change may turn peatlands into a net source of carbon. Peatland restoration, through the EU Life Programme (2001 -2005) and more recently by the RSPB in the Dyke catchment, has been adopted to restore part of the Flow Country disturbed peat bogs to their pre-disturbance state in order to encourage more C storage. However, very little is known about the influence of afforestation and/or deforestation on the export mechanisms and dynamics of dissolved organic carbon (DOC).

This research was fundamentally motivated by a need to increase the datasets documenting aquatic C losses in the Flow Country peatland systems and our understanding of the impact of landuse change on DOC, and therefore a a comprehensive plot-scale storm event-based monitoring programme was undertaken. This study provides insight into the catchment-scale chemical, biological, physical and hydrological processes and their impacts on DOC release to streams in the intact, forested and restoring plots of the Dyke catchment. This concluding chapter summarises the main research findings and discusses the main controls on DOC export that were investigated in Chapters 4 - 8. Major limitations, both practical and theoretical, associated with sampling programme and applied methods are discussed, and areas of future research are highlighted. The approaches adopted in this study have proved beneficial in understanding the export mechanisms of DOC and effects of landuse change in the Dyke catchment, and recommendations on better landuse practices are suggested in order to mitigate future climate-change impacts on DOC exports.

As this research focuses primarily on the landuse change factor, the results are applicable to upland catchments with similar characteristics.

9.1. Summary

This study has attempted to assess the discharge-DOC relationship in order to understand the spatial and temporal variability in DOC concentrations. Spatial and temporal variability in streamwater chemistry in terms of DOC, metal ion and base cation concentrations has provided insights into catchment response to changing conditions related to rainfall and temperature. The aims and objectives of this study have been achieved by means of intensive sampling programmes during storm events, flows before and after the storm events, and base flows. Preferential hydrological pathways were delineated during storm events at individual sites, and conceptual models illustrating periods of high DOC exports (EMMA), and the export mechanisms of DOC (conceptual diagrams) for individual sites, are proposed. Using the discharge-temperature-DOC relationship, time-series of DOC concentrations were developed for each site in order to compute DOC loads from individual study sites, and from the Dyke catchment as a whole.

9.1.1. Main research findings

The following sections outline the major findings in this research with respect to the objectives set out in Chapter 1.

Objective 1: Monitoring background levels of stream water chemistry and investigating the spatial and temporal variability in DOC concentrations for the three sub-catchments.

In this study, remarkable differences in the stream water chemistry between the sites were found. Streamwater at the intact site is generally low in conductivity,

base cation concentrations, while that at the forested and felled sites are characterised by relatively high concentrations of the same parameters, probably due to relatively high amount of underlying glacial till and alluvium (Langan *et al.*, 1995) in the latter sites. Although, bedrock geology is relatively homogenous across the sites, spatial variability in the streamwater chemistry suggests local variations in the bedrock weathering rates (Nezat *et al.*, 2004) and mineralogy. Of all the sites studied, streamwater from the felled site is acidic and has high mean conductivity and base cation concentrations reflecting the effects of soil structure disturbance due to felling; these high concentrations are possibly arising due to increased rates of bedrock weathering and cation exchange mechanisms locally.

Mean DOC and metal ion concentrations are generally low at the intact site, and relatively high at the felled site, while intermediate concentrations are seen at the forested site. The oxidation of metals like Fe, Mn and Al is relatively slow under acidic conditions (Stumm and Morgan, 1996), and reduced forms of these ions are more soluble than their oxidized forms (Laxen and Chandler, 1983). Hence, relatively high mean pH at the intact site could possibly explain the low metal ion concentrations in the streamwater at this site. Similarly, at the forested site, intermediate pH and high dissolved oxygen due to active photosynthesis could be responsible for the observed intermediate concentrations of DOC and metal ions in streamwater. In contrast, low pH, high DOC and low dissolved oxygen concentrations at the felled site suggest that redox processes are primarily responsible for the supply of metals like Fe and Mn, which form complexes with DOC, and are mobilised by DOC in streamwater (Graham *et al.*, 2002; Tipping *et al.*, 2002; Björkvald *et al.*, 2008; Baken *et al.*, 2011). Therefore, at the felled site, the soil disturbance due to felling and the additives used on the forestry (before felling) are re-exposed to interact

with flowing water, which are reflected in relatively high concentrations of base cations, metals and DOC (Cummins and Farrell, 2003a, 2003b).

The findings in this study suggest that spatial variability in stream water chemistry is mainly controlled by catchment characteristics such as bedrock (weathering rates), superficial geology, and landuse.

Objective 2: Investigating flow related variability in stream chemistry during hydrological events, in order to assess the contribution of different runoff source areas to stream flow during those events.

During storm events, variability in streamwater chemistry related to changes in discharge is distinct for each site in terms of concentration and magnitude of change, and the timing of peak concentrations. Streamwater chemistry variations are conceptualized as being the result of varying hydrological pathways during events, which is confirmed by the variability in determinants that are characteristic of different flowpaths.

The results from Q- and R-mode factor analysis indicate that two important possible factors (flow paths) can explain about 71 - 79% of the variance in the stream chemistry data. It has been demonstrated that during the events, the main flow pathways switch from deeper sources rich in base cations, to shallower organic soil sources rich DOC and metal ions. These results were used to develop an end-member mixing model (EMMA), which is used for predicting the hydrochemical stream response to storm runoff events and to identify critical periods of DOC and metal exports to streams.

The results from EMMA show that soilwater has a greater influence on the stream chemistry with the proportions rising up to 65% during high flows and an associated dilution of the groundwater signal. However, groundwater

inputs also show an increase during high discharge, reaching as much as 40 - 50% of the total stream discharge and buffering the stream chemistry. At the intact site, the onset of an event is characterized by water from overland and shallow surface sources, which are greater than groundwater inputs from deeper sources within 2 hours of an event onset. At the forested site, end-member modelling suggests that the stream receives inputs from 1) rapid (surface, shallow) flowpaths until the time of peak flow, followed by 2) organic-rich soilwater sources immediately after the hydrograph peak, and finally 3) near-stream deep soil or groundwater sources on the receding limb of the hydrograph (Brown *et al.*, 1999). At the felled site, a mechanism similar to that observed in the forested site is evident, however, disturbance to the soil structure due to felling, and decomposition of felled tree litter in the felled site, result in differences in streamwater chemistry between the two sites.

The EMMA modelling results suggest that although soilwater contributes predominantly during storm events, groundwater is the dominant contributor to stream discharge throughout the year, and the relative proportions of groundwater declines during peak discharges. However, at the felled site, relatively high proportions of groundwater compared to other sites could be due to the presence of drain blocks and felled tree litter, which resist surface and subsurface runoff and delay the release of water, thus allowing for percolation to increase groundwater storage. Similarly, at the forested site, the presence of the tree stand and litter reduce surface runoff and aid percolation of water to deeper soil sources, hence the proportion of groundwater or deep soilwater seems to be relatively high when compared to the intact site. Therefore, the spatial and temporal changes in streamwater chemistry in relation to discharge is a function of hydrologic pathways of water, as the

varying concentrations of these elements indicate differences in the residence times of water reaching the streams.

The results from the hydrograph separation identified the flowpaths of water that are important in understanding the catchment processes such as overland flow, subsurface runoff, and erosion as these processes mobilize nutrients, organic carbon and associated metal ions. The derived EMMA model also satisfactorily explained the influence of land-use factors in terms of lags in stream chemistry, differences in hydrologic flow paths, and catchment responses to storm events (depending on the antecedent moisture conditions), which are in agreement with the findings of factor analysis.

Objective 3: Establishing principal differences in DOC concentration ranges between undisturbed (intact) and disturbed (forested and felled to waste) sites in the catchment.

DOC concentrations exhibit spatial variability with higher concentrations generally occurring in the streamwater from the felled site (8 - 80 (± 9.6) mg C L^{-1}). Sometimes, these concentrations are nearly two times greater in magnitude than that observed at the forested (2.5 - 42 (± 8.3) mg C L^{-1}) or intact (4 - 44 (± 5.0) mg C L^{-1}) sites. In the UK uplands, DOC concentrations are influenced by seasonality with maximum values generally associated with summer and autumn (Grieve, 1990a; Proctor, 1994; Clark *et al.*, 2004; Dawson *et al.*, 2011), and such seasonal variations in the DOC concentrations were found to be larger than those due to storms and those between catchments (Grieve, 1990a). In this study, DOC concentrations show strong seasonality at all three sites, with higher concentrations and fluxes evident during summer months followed by autumn and finally winter.

Particulate organic carbon (POC) concentrations range from 0 to 21.3 (± 6.7) mg C L^{-1} at the intact site, 0 to 15.5 (± 1.8) mg C L^{-1} at the forested site, and 0 to 17.4 (± 2.3) mg C L^{-1} at the intact site; higher concentrations are generally associated with summer storm events. Higher concentrations (and variability) at the intact site, given its topography and relatively steeper slope that may provide energy for stream runoff, probably suggest relatively higher rates of erosion compared to the other two sites. The Dyke catchment is a DOC - dominated peat catchment with DOC accounting for > 90% of total carbon, while POC concentrations account for only 6 -10% of total organic carbon.

Objective 4: Examining DOC relationships with discharge, and identifying the sources and major flowpaths of DOC in the catchment.

A significant positive correlation between DOC and discharge has been reported by several studies (McDowell and Likens, 1988; Reid *et al.*, 1981, 1981; Worrall *et al.*, 2002, 2008). However, the relationship can sometimes be weak (Tipping *et al.*, 1988; Bishop *et al.*, 1990; Grieve, 1991) and even inverse (Clark *et al.*, 2008) depending on the availability of removable DOC and time gap between the events (Worrall *et al.*, 2006). Similar to many upland catchments (Tipping *et al.*, 1988; Grieve, 1994; Hope *et al.*, 1997a), a significant positive correlation between DOC and discharge is evident from the data, however, these relationships vary between seasons (Ågren *et al.*, 2008; Dawson *et al.*, 2008). Following the flushing of available DOC in late summer and autumn months, coupled with relatively reduced production of removable DOC (Brooks *et al.*, 1999) during winter months, lowers DOC concentrations in the stream water for a given discharge. Subsequently, soil biological activity appears to rise during spring, due to increase in temperatures, resulting in increased DOC concentrations in stream waters. Thus, while discharge explains

40-70% variability in DOC concentrations in all three sites, it explains less than 15% of DOC concentration for the spring period. In this study, POC did not show significant relationship with discharge in the studied sites.

Sources of DOC

Dissolved organic carbon concentrations in precipitation are generally low, between 0.5 and 2.6 mgC L^{-1} (Likens *et al.*, 1983; Wilkinson *et al.*, 1999; Neal *et al.*, 2005). Given the high mean DOC concentrations in the sub-catchments in this study, inputs from atmospheric sources are small relative to the internal fluxes.

The Dyke monitoring sites are on lower order streams, therefore the majority of exported organic carbon appears to be derived from (allochthonous sources) decomposing peat, vegetation and leaf litter, felled tree litter, and leaching and erosion of soil organic matter (Thurman, 1985; Hongve *et al.*, 2000; Billett *et al.*, 2006; Hood *et al.*, 2006). The lower E_4/E_6 values (5 - 12) that occur during storm events suggest that the majority of the DOC exported during the events is relatively younger (Thurman, 1985).

Several studies have found a significant decrease in DOC concentrations and fluxes with increasing soil depth (McDowell and Likens, 1988; Moore, 1989; Grieve, 1990b, 1990c; Hiederer, 2009). In this study, in general, DOC concentrations in the peat profile were found to increase up to a depth of 100cm, probably due to increased aeration at depths < 100 cm and more production of DOC within this depth during summer months in particular; concentrations then decrease at greater depths. However, the concentrations vary with soil thickness and water content across the catchment.

Carbon isotope studies in similar catchments have indicated that the majority of DOC in streamwater is young and less than 40 years old (Schiff *et*

al., 1997; Billett *et al.*, 2006, 2007). Based on E_4/E_6 ratio (absorbance at 465nm to that at 665nm) analysis, it is evident that relatively young DOC dominates the higher concentrations during the storm events, while comparatively mature DOC at discharge peaks support the contribution of water from deeper sources (see *Figures 7.17 - 7.19* in chapter 7). Results from E_4/E_6 analysis also suggest that DOC in the Dyke catchment is mainly derived from the upper organic horizons (< 50cm depth) of peat (Worrall *et al.*, 2002; Moore, 2003; Billett *et al.*, 2006; Clark *et al.*, 2008). The intact site seems to have relatively more mature DOC compared to the other sites. DOC in the forested and felled sites is relatively young or less mature as a constant supply of fresh organic matter (leaves, twigs or litter from felled trees) is added regularly to the C pool in these sites.

Major flowpaths of DOC

Significant changes in the flow paths of water moving through the soil occur during storm events, dependent on soil type (Wheater *et al.*, 1993; Clark *et al.*, 2008), with the majority of flow occurring through the upper soil horizons (Bishop *et al.*, 1990; Evans *et al.*, 1999; Holden and Burt, 2003). Moreover, rapid movement through these upper peat horizons (Brown *et al.*, 1999) allow DOC-rich water to bypass adsorption sites in the lower soil horizons (Moore, 1989). The results of the end-member mixing (EMMA) modelling show that the flowpaths during storm events are mainly a mixture of soilwater and groundwater, and DOC is mainly derived from the soilwater component from within a depth of 50cm in peat profile. This is in agreement with similar studies on DOC exports (Hinton *et al.*, 1998; Billett *et al.*, 2006; Clark *et al.*, 2008; Wallage and Holden, 2010).

Objective 5: Investigating possible export mechanisms and developing conceptual models of DOC export.

Storm event analysis of DOC highlights hysteresis that varies for each site. DOC hysteresis possibly is one of the reasons for the observed weaker DOC - discharge correlations. Clockwise hysteresis (DOC peaks prior to discharge peak) is dominant in the intact site and anti-clockwise hysteresis (DOC peak lags behind the discharge peak) is predominant in the forested and felled sites, indicating different mechanisms of DOC export based on which conceptual models for disturbed and undisturbed sites proposed.

Based on the findings from EMMA, E_4/E_6 ratio, and hysteresis analyses, conceptual models are proposed for the sites, which explain the mechanisms of DOC export during storm events. Each model is classified into four stages to represent early, rising, peak, and receding stages of a hydrograph. At the intact site, increasing concentrations of DOC and metal ions in the initial stages of hydrograph suggest the dominance of soilwater in the stream flow. However, timing of peak concentrations and hysteresis loops were found to be different for DOC and metal ions (Fe, Mn, Al and Ti) suggesting different sources, and a near-surface source for DOC was confirmed by E_4/E_6 analysis. At the onset of an event, streamflow is therefore characterised by inputs from overland and shallow surface sources with high DOC concentrations. At peak discharges, saturation excess runoff or shallow subsurface flow depleted in DOC mixes with soilwater from deeper sources (with relatively longer residence times) that are rich in ions such as Fe, Mn, Al, and Ti dominate the stream flow. In the later stages of hydrograph, groundwater sources are dominantly input to the stream buffering the stream chemistry by increasing concentrations of weathering-derived base cations.

At the forested and felled sites, riparian water (with longer resident times) rich in base cations, Fe and Mn seems to dominate the earlier stages of the storm

hydrograph gradually giving way to soilwater during the later stages, suggesting 'displacement of pre-event water' in the riparian zone (Giusti and Neal, 1993; Kendall and McDonnell, 1998; Inamdar *et al.*, 2004). At peak discharges, the lags observed between peak discharge and peak concentrations of DOC suggest a possibility of macro-pore flow or flow through preferential pathways (roots zones, pipes etc.) with relatively less residence times and minimal interaction with available DOC-rich sources dominate the stream discharge. In these sites, DOC peaks are seen in the later stages of the hydrograph, where shallow-subsurface event water with relatively longer residence times and enriched in DOC, tend to dominate the stream flow. At this stage, DOC is flushed from the acrotelm followed by increasing post-event water from deep soil or groundwater sources in the later stages of the hydrograph.

Objective 6: Quantifying organic carbon exports in a nested approach (from each sub-catchment and from the whole Dyke catchment), and assessing landuse change impacts on organic carbon loads.

Time-series of DOC concentrations developed using continuous discharge and water temperature data proved useful in estimating total annual DOC loads from the catchment. Total organic carbon exports from the forested site are higher compared to the other sites because it has a larger area, while organic carbon release per unit area is the highest from the intact site (943 ± 59 kg C ha^{-1} $year^{-1}$).

Comparison of organic carbon loads from the Dyke catchment for the same period in 2009 and 2010 illustrates an overall decrease of 13% following a 5% increase in total discharge and a 7% decrease in average temperature. Observed decrease in DOC loads (in 2010) is probably due to limited

availability of removable DOC, or a reduced rate of DOC production due to decrease in temperature. For the same period at the intact site, 52% increase in total discharge resulted in about the same amount of increase in DOC loads, reflecting a relatively large labile and accessible organic C pool. Similarly, 5% increase in total discharge at the forested site results in a 10% rise in DOC loads. The felled site, unlike the other two sites, exhibits an 11 % drop in DOC loads despite a 5% rise in total discharge, which probably reflects the effectiveness of drain blocks in limiting DOC loads (Wallage *et al.*, 2006; Worrall *et al.*, 2007; Gibson *et al.*, 2009).

Landuse change effects

This study hypothesized that organic carbon concentrations and fluxes from the disturbed catchments, i.e., forested and felled-to-waste plots, is relatively higher than that from the undisturbed (intact) site. The following summary table *(Table 9.1)* gives the major distinguishable characteristics (in terms of organic carbon) comparable between the different landuse sites.

At the intact site, the increase in the amount of DOC released to the stream, or the higher DOC yield of 943 kg C ha^{-1} $year^{-1}$, demonstrates that it exports a higher yield of organic carbon (Aitkenhead *et al.*, 1999). Differences in the discharge and DOC exports for the sites, assuming the same amount of precipitation is received for each sub-catchment monitoring site, appears to be a function of water yield. Hence, lower water yield of forested and felled sites during the study period resulted in lower annual DOC exports (403 kg C ha^{-1} $year^{-1}$ and 700 × 10^3 kg C ha^{-1} $year^{-1}$ respectively) from these sites.

Table 9.1: A summary table showing the major differences (in relation to organic carbon) between the undisturbed(intact) and disturbed (forested & felled-to-waste) sites.

	Intact	***Forested***	***Felled***
Mean groundwater (GW) and soilwater (SW) proportions.	GW%: 55.3 (±1.2) SW%: 44.7 (±1.23)	GW%: 56 (±1.2) SW%: 44 (±1.19)	GW%: 62 (±1.5) SW%: 38 (±1.5)
Mean DOC concentrations (mg C L^{-1}).	13.7 (± 0.05)	14.6 (± 0.04)	36.6 (± 0.1)
Mean POC concentrations (mg C L^{-1})	1.95 (± 0.2)	1.5 (± 0.12)	2.2 (± 0.15)
DOC export mechanism during storm events	• DOC-rich event water from within the top 50 cm of peat, peaks before pre-event water. Hence, high DOC concentrations occur during earlier stages of storm hydrograph.	• Event water with relatively longer residence times (enriched in DOC) is lagged behind pre-event water and is released to stream during later stages of storm hydrograph.	• Event water, held back by drain blocks, is enriched in DOC and is lagged behind pre-event water; and is eventually released to stream during later stages of storm hydrograph.
DOC fluxes (kg C ha^{-1} $year^{-1}$)	942.9 (± 59)	403.3 (± 65)	700.1 (± 107)
POC fluxes (kg C ha^{-1} $year^{-1}$)	81.7 (± 18)	27.4 (± 11)	34.9 (± 16)
*Quality of DOC (E_4/E_6 * ratio)*	4.2 - 5.6	4.3 - 9.7	6.3 - 16.5

* from within the top 50 cm of peat. The higher E_4/E_6 value suggests younger or relatively less mature DOC; and low E_4/E_6 is indicative of relatively mature DOC.

Results show that climate-related changes in rainfall (indirectly to discharge) and temperature are the main controls on DOC release. Although, increase in temperature would not necessarily lead to an increase in DOC, it may lead to increase in DOC productivity and hence the combination of warming and drying cycles may lead to increases in DOC export (Tipping *et al.*, 1999).

DOC load estimates suggest that in the Dyke catchment (522 kg C ha^{-1} $year^{-1}$), landuse change associated with afforestation and restoration by felling-to-waste and re-wetting does not appear to have significant impact on DOC release over the time period of this research (2009-2011). For example, in the case of afforestation, Grieve (1990b) found little difference in DOC concentrations exported from a forested and a moorland catchment, except during peak discharges. Evidence from the analysis of hydrological pathways suggests that the main differences in landuse are due to the changes in preferential flowpaths and hence different DOC export mechanisms. However, differences in DOC fluxes may be due to the different water yield capacities of individual catchments (Gibson *et al.*, 2009), which result in varying discharges. Therefore, total annual organic carbon loads from the Dyke catchment are a function of climate-related changes in terms of discharge, precipitation inputs, temperature (seasonality) and water yield rather than landuse change.

The calculated annual fluxes of DOC from the Dyke and Halladale catchments, up-scaled from the results of the individual sub-catchments, are 521.6 and 647.9 (± 65) kg C ha^{-1} yr^{-1} respectively, which are significantly (~5-6 times) higher than the previously published value (103.4 ± 25 kg C ha^{-1} $year^{-1}$) for the River Halladale catchment (Hope *et al.*, 1997b). In this study, it has been shown that 57 - 95% of the DOC export occur during the upper 5 - 10% of the high discharges, therefore, it is crucial that quantitative records of DOC export

are developed using high frequency storm event measurements, as well as lower frequency low flow sampling.

9.1.2. Limitations

The results presented in this study are applicable to blanket peats, which have undergone landuse change by afforestation and restoration (felled-to-waste). However, the ultimate response of individual catchments will depend on its fundamental characteristics soil type, drift and bedrock geology, and topography. Hence, additional research is required in order to determine whether the same processes operate in other catchments undergoing the same landuse treatments.

The main practical limitation of this study was identified in the data collection. Intensive data collection was limited in winter and autumn months during which access to the sites was impossible because of thick snowdrifts and during deer hunting/counting periods. This resulted in under-representation of the data from winter and autumn months, although spot samples were collected during this period whenever possible.

In addition, limitations in the end-member mixing model (EMMA) for predicting hydrochemical stream response to storm events mainly occur due to the assumptions required by the method (see Chapter 6), and the application of a simplistic two-component mixing model (as a first approximation), while DOC variability reflects a third component (a shallow-water component). However, the understanding gained from the EMMA was integrated with soil pore-water DOC and absorbance (E_4/E_6) analysis results, before developing conceptual models for DOC export mechanism for sites.

The results from EMMA model using Ca and Mg as tracers was successful in identifying important flowpaths during storm events and critical periods of high DOC and metal loadings. Yet, it has limitations in quantitatively predicting DOC or other soilwater chemical parameters in the streamwater, which may be improved further by coupled use of geochemical and isotope tracers to better represent the end-members.

Further limitations arise due to the estimation of DOC concentrations from continuous discharge and water temperature data. This may lead to an overestimation of DOC as the concentrations were determined from the continuous discharge data (Hobbie and Likens, 1973; Edwards *et al.*, 1984), and increase in discharge does not always result in high DOC concentrations, especially when the storm events are closely spaced (Worrall *et al.*, 2002). However, the predicted and measured concentrations were strongly correlated ($R^2 = 0.93$, $p<0.001$) and the resultant residuals were very low. However, total uncertainty (95% confidence intervals) in the computed loads, due to DOC concentration and flux estimation methods used, varied between ± 5% to ± 16%. Uncertainties in this study can be considered as of a lesser degree when compared to other similar studies (for example, Hope *et al.* (1997a) and Worrall *et al.* (2009), these are based on regular but less frequent sampling), since the DOC concentrations in this study were measured at a relatively high frequency during storm events, in between events, and during low flow conditions.

Finally, other limitations occurred due to the malfunction of equipment, and particularly, the pressure transducers and automatic water samplers failed to operate sometimes which resulted in more limited data collection than expected.

9.1.3. Recommendations for Future Research

This study provides the base line water chemistry for different landuse practices in the Dyke catchment, and insight into hydrological, physical and chemical processes responsible for DOC export. There is a great potential for extending the work undertaken in order to further advance our current understanding of the key processes operating in the catchment. The recommendations for any future monitoring in the catchment are given as follows:

1. Include more frequent and extensive collection of water samples from the sites to represent different times of the year sufficiently. An integral part of the future sampling initiatives should be sampling a series of continuous storm events to assess variability in DOC with respect to antecedent soil-moisture conditions and changes in hydrological pathways.

2. Soil porewater samples should be collected more frequently, especially from the shallow layers of peat (< 30cm), in order to confirm the source of DOC from these parts. Additional rainwater, throughfall and runoff samples need to be collected and analysed as required to better characterise the end-member concentrations and improve the reliability of the EMMA model. This would facilitate the estimation of DOC or associated metal concentrations quantitatively, supported by detailed catchment studies on soilwater and groundwater chemistry and distribution.

3. Oxygen isotope studies on the water samples would enable an investigation of the release of 'old water' and 'new water' to streams

during events, which would further help in understanding the mechanisms, sources and pathways of DOC export more reliably.

4. Soil cores from each site should be collected in order to estimate the peat depth and available organic carbon pool in the catchment, for which only limited data are available.

5. Data from the above recommendations can be coupled with additional carbon release pathways, such as gaseous fluxes (CO_2, CH_4), and inorganic carbon fluxes production and release, to complete a soil-stream-atmosphere total carbon budget for the catchment.

9.2. Concluding Remarks

The results presented in this research offer an insight into the processes controlling the DOC dynamics in the Dyke catchment, and the impact of disturbance caused by landuse changes such as afforestation and tree-felling for restoration. This will eventually help improve our predictions related to future climate change and landuse change in the peatland systems. In addition, the results from this study provide landowners, policy makers and organisations such as RSPB with the evidence they require for initiating future peatland restoration works, as felling of forestry coupled with drain-blocking is shown to be losing as much or less organic carbon and associated metals as an intact site in terms of annual yields. However, it still needs to be understood as of which method of restoration (for example, removing trees after felling, felling trees-to-waste etc.) would be beneficial in terms of exposure and release of nutrients into streams. Therefore, further investigation on effective restoration techniques, felling of forestry and blocking the drains in the catchment may help the catchment to eventually return to a near-pristine state. The results of

this research may be used to infer that the Dyke catchment restoration plots may be approaching this state already. Since this study was initiated well after the felling stage in the Dyke catchment, it is unclear whether the relationships and conclusions stated here apply to the immediate response of the catchment to felling. Although restoration techniques help improve the storage potential of these carbon stores, nutrients like nitrates and phosphates are not accounted for in this study and their mobilisation for the different land usages also needs to be investigated. This study has identified key processes and changes in hydrological pathways that control DOC release from different landuse treatment sites, which can be useful for future monitoring in the catchment or applicable to catchments with similar catchment characteristics.

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Appendix I. Water Analysis methods

pH

pH is a measure of the acidity or basicity of an aqueous solution and is mainly controlled by the dissolved species and their interactions in the solution. In simple, it is defined as the logarithm to base 10 of the reciprocal of the hydrogen ion,

$$pH = -\log_{10}(a_{H+})$$

Where a_{H+} is the activity of hydrogen ions in the solution expresses in mol L^{-1}.

pH is measured *in situ* at each site using HachLange HQ30D pH electrode which has a detection limit of 0 - 14 pH units, with an accuracy of ± 0.002.

Conductivity (specific conductance)

It is a measure of the ability of an aqueous solution to conduct an electric current and is generally defined as the reciprocal of the resistance measured between two electrodes unit distance apart with a unit cross-sectional area. Therefore, it depends on the dissolved solids in the solution, mostly mineral salts, and on the degree to which those salts dissociate into ions. Generally, temperature influences the conductivity of a material, therefore measurements are corrected to room temperature (25^0c) so that differences in conductance are only a function of the type and the concentration of the dissociated ions.

Specific conductance (at 25^0C) is measured *in situ* at each site using HachLange HQ30D conductivity electrode, which has a detection limit of 0.01µS/cm – 200 mS/cm with an accuracy of ± 0.5%.

Dissolved oxygen (DO)

Dissolved oxygen of an aqueous solution is a relative measure of the amount of oxygen that is dissolved or carried in the solution. Since it is

influenced by temperature changes, dissolved oxygen concentrations are generally reported as temperature-corrected values in mg/l.

Dissolved oxygen is measured *in situ* at each site using HachLange HQ30D LDO electrode, which has a detection limit of 0.00 – 20.0 mg/l; 0-200% with an accuracy of ± 1%.

pH, conductivity and DO readings by HachLange probes are measured in temperature corrected (25^0C) units.

Absorbance

Absorbance of an aqueous solution is a logarithmic measure of the amount of light absorbed, at a particular wavelength, as the light passes through the sample.

$$A_\lambda = \log_{10}\left(\frac{I_0}{I}\right)$$

Where,
A_λ is the absorbance at wavelength λ
I_0 it the intensity of the light before entering the sample,
I is the intensity of light at a specified wavelength λ

Absorbance values are used as a proxy to dissolved organic carbon (DOC) concentrations in water samples, since it is proportional to the concentrations of the absorbance species (such as humic acids in DOC). Absorbance of water samples are measured using Hach DR 2800™ Portable Spectrophotometer, which has a wavelength range of 340 to 900 nm, accuracy of ±0.002 at 0.0-0.5 Abs and 1% at 0.5 - 2.0 Abs.

This study used a multi-wavelength mode in which absorbance values are measured at four wavelengths, 360, 400, 465, and 665 nm. The amount of light absorbed by water samples is given in units of absorbance. Water samples are taken in a clean 1-inch quartz sample cell and inserted into the sample cuvette of the spectrophotometer. Measurements are made following the onscreen

instructions. Prior to each measurement, a sample cell with de-ionised water (a blank) is used to zero the absorbance reading on the instrument, this is to ensure minimal drift in the readings.

Particulate organic carbon (POC)

Particulate organic carbon concentrations in sediment left on filter papers were analysed using the loss-on-ignition method. Filter papers and sediment were initially oven dried at 105^0C for 12 hours to eliminate hygroscopic water and ensure accurate sediment weight measurements (Eaton et al., 2005). Samples were then combusted in a pre-heated muffle furnace at 550^0C for 4 hours (Christensen and Per Åkesson Malmros, 1982; Eaton et al., 2005; Heiri et al., 2001; Lyons et al., 2002; Sarkhot et al., 2007) and weight loss on ignition was determined on the combusted samples. With each batch of samples, two blank filter papers were analysed to account for the weight lost by filter paper (W_{FB}) during combustion. Organic matter weight lost on ignition was corrected using W_{fb}. POC content was estimated based on the assumption that organic carbon accounts for 58% of the organic matter weight reduction following combustion (Ayub and Boyd, 1994; Broadbent, 1953; Nelson and Sommers, 1996; Sarkhot et al., 2007). POC concentration was computed using the following equations:

$$W_{105} - W_{550} = W_L \quad \ldots\ldots\ldots\ldots \quad (Eq.\ 0.1)$$

$$W_L - W_{FB} = W_{LOI} \quad \ldots\ldots\ldots\ldots \quad (Eq.\ 0.2)$$

$$W_{POC} = 58\% * W_{LOI} \quad \ldots\ldots\ldots\ldots \quad (Eq.\ 0.3)$$

Where,

W_{105} = Weight after oven drying at 105^0C for 12 hours

W_{550} = Weight after combustion at 550^0C for 4 hours

W_L = Total weight lost after combustion

W_{FB} = Weight lost by filter paper (blank)

W_{LOI} = Total weight of organic matter lost after ignition

W_{POC} = Weight of particulate organic carbon

ICP-MS analysis

The analysis of major, minor and trace elements (such as Ca, Na, Mg, K, Al, Fe, Mn, Ti, Ni, Cu, Cr, Zn and V) in water samples is carried out using a Thermo X-series® Inductively Coupled Plasma Mass Spectrometer (ICP-MS) at St Andrews. This method uses a high energy and temperature (up to 10000K) Argon Plasma as an excitation source to atomise and ionise elements in a solution, which is introduced through the plasma by means of an aerosol (Jarvis et al., 1992). The ions from the plasma are extracted through a series of cones into a mass spectrometer, where the ions are separated based on their mass-to-charge ratio and a detector receives an ion signal proportional to the concentration of the analyte.

The concentrations of the analytes of in a sample are computed directly by the spectrometer through calibration with certified reference standards. During calibration, the correlation coefficient was calculated for each element to assess the quality of calibration. To be considered acceptable, correlation coefficient of a calibration curve should be greater than or equal to 0.998 (SW-846 On-Line, 2007), therefore, in this analysis with a multi-point calibration approach every effort was made to attain an acceptable correlation coefficient. After satisfactory calibration of the instrument, the samples were analysed, during this method each sample was analysed as a replicate of three from which the mean intensity and concentration (C) values of the analytes were derived (Jarvis et al., 1992). Standard deviations (SD) and the relative standard deviation (RSD) were automatically calculated using the following equations (Abesser, 2003):

$$SD = \sqrt{\frac{\sum(C_i - C_{mean})^2}{n-1}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (Eq\ 0.4)$$

$$RSD = 100 \times \frac{SD}{mean} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (Eq\ 0.5)$$

Table I-1: Range and precision (% relative standard deviation) of the analyte concentrations computed by ICP-MS. Shown in ppb (equ. µg/l).

Analyte	Minimum	Maximum	Mean	Std Dev	%rsd
Na	7554.0	21912.0	20772.3	831.4	4.0
K	1957.0	2100.0	2021.7	148.6	7.4
Mg	135.0	8299.0	7909.4	743.2	9.4
Ca	38.0	31960.0	31443.0	756.4	2.4
Al	135.0	145.0	140.1	9.9	7.1
Fe	62.5	98.9	98.0	1.7	1.7
Mn	38.3	39.5	38.6	1.0	2.5
Zn	60.1	79.0	78.0	1.7	2.1
Ni	20.2	63.4	62.9	0.9	1.5
Cu	20.2	22.8	21.4	2.5	11.7
Ti	6.6	8.0	7.2	1.3	18.2
V	20.3	39.0	38.2	1.6	4.2
Cr	20.3	21.9	21.0	1.8	8.4

Although calibrations for most of the elements fall within the range, however, for the elements like, P, S, Pb, Zn, Cu, V, As and Sn the RSD exceeded 5% , hence these elements are not included in any further analysis. The concentrations are reported as ppb (parts per billion, equivalent to µg/l) for elements like Al, Fe, Mn, Ti, Cu, Zn and ppm (parts per million, equivalent to mg/l) for Ca, Mg, Na, and K by the ICP-MS system. Precision and lower detection limits of the analyte concentrations measured using ICP-MS method are listed in *Table I-1 & Table I-2.*

Table I-2: Lower detection limits of some of the elements analysed by the Thermo X-series ICP-MS system.

Analyte	**Detection limit (in ppb)**
Aluminium (Al)	0.02
Calcium (Ca)	0.6
Chromium (Cr)	0.005
Copper (Cu)	0.002
Iron (Fe)	0.9
Magnesium (Mg)	0.02
Manganese (Mn)	0.008
Nickel (Ni)	0.003
Potassium (K)	2
Sodium (Na)	0.2
Titanium (Ti)	0.01
Vanadium (V)	0.003
Zinc (Zn)	0.02

Appendix II. Discharge Measurements

Discharge measurements at the gauging sites were undertaken under different flow conditions during the study period (August 2009 – April 2011) using a Valeport open channel flow meter. The specifications are given in the table below.

Table II-1: Specifications of Valeport Open Channel Flow Meter - Model 001 and equations used to compute stream discharge

Type	8011 series High Impact Styrene Impeller
Size	125 mm diameter by 270 mm pitch
Range	0.03 to 10 m/s
Accuracy	± 1.5% of reading above 0.15 m/s ± 0.004 m/s below 0.15 m/s
Calibration used for velocity (V)	for n = 0.1 - 1.5 rev/s, $V = 0.032 + 0.1001 \times n$ for n = 1.5 - 29 rev/s, $V = 0.030 + 0.1079 \times n$ n=number of rotations of the impeller
Cross-sectional area (A) of stream channel	A = Width of the segment × Depth of the water column (see *Figure II-1*)
Discharge (Q)	A × V A = area of cross-section of the stream channel

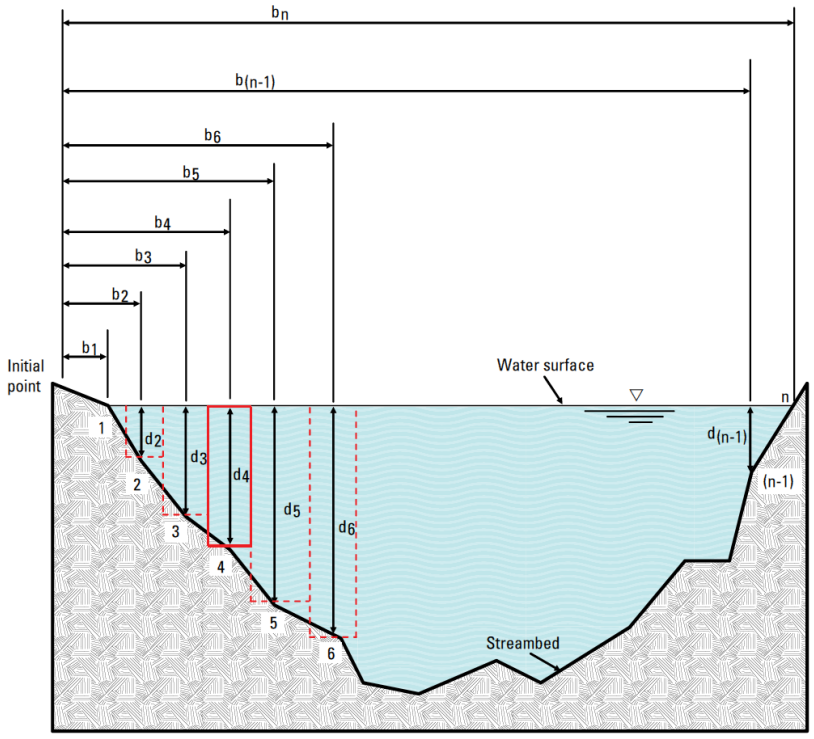

Figure II-1: Sketch showing 'mid-section' method of calculating cross-section area (A) for discharge measurements.

1, 2, 3, 4…..n - observation points
b_1, b_2, b_3,……b_n - distance between the initial point and the observation point
d_1, d_2, d_3,……d_n - depth of water column at the observation point

(Figure taken with permission from Turnipseed and Sauer, 2010)

Cross-sectional area of stream channel is calculated using 'mid-section' method shown in *Figure II-1*. Flow velocity measurements are generally made at each segment using a two-point method where the depth of water column is > 0.76m and using a six-tenths depth method where the depth is < 0.76m. These methods are described in detail in Turnipseed and Sauer (2010). For all the gauging sites, water depth was always under 0.7 m during the measurements, hence the 'Six-tenths-depth' method was used. In this method, the flow meter impeller is placed at 60% of the depth below water surface, thus flow velocity at that depth is used as mean velocity in the vertical segment.

Table II-2 & Table II-3 show the discharge values computed from the flow measurements made at the intact and forested sites respectively. Only three measurements were made at the felled site, which were not satisfactory as the channel was relatively instable and water was stagnant at times, therefore not included here. Discharge - stage relationships used to develop continuous discharge data for the sites are shown in *Figure II-2.*

Table II-2: Discharge measurements and corresponding stage level at the gauging point of the intact site.

Date & Time	Stage (m)	Discharge (m^3/s)
22/08/2009 11:15	0.28	0.036
25/04/2010 11:30	0.27	0.021
26/04/2010 09:50	0.3	0.074
27/04/2010 10:35	0.26	0.013
26/08/2010 09:30	0.28	0.025
28/08/2010 08:50	0.22	0.01
04/04/2011 10:10	0.278	0.034
07/04/2011 09:35	0.35	0.069

Table II-3: Discharge measurements and corresponding stage level at the gauging point of the Forested site.

Date & Time	Stage (m)	Discharge (m^3/s)
05/08/2009 13:00	0.195	0.07
24/04/2010 18:10	0.375	0.636
25/04/2010 15:35	0.268	0.222
26/04/2010 15.40	0.295	0.266
27/04/2010 14.25	0.251	0.141
28/04/2010 10:30	0.4	0.68
26/08/2010 10:40	0.29	0.163
28/08/2010 09:50	0.24	0.070
04/04/2011 12:45	0.295	0.169
07/04/2011 10:25	0.4	0.577

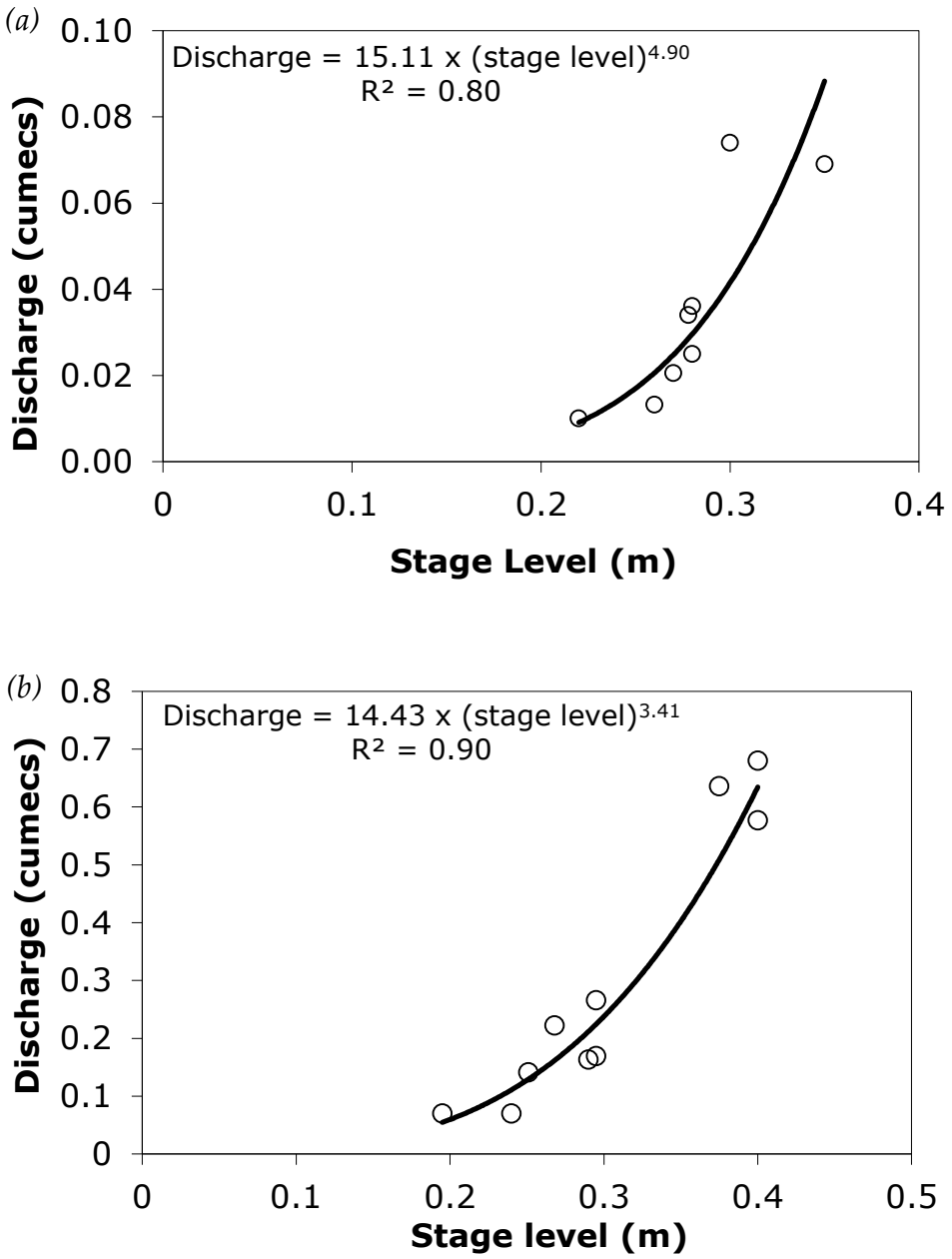

Figure II-2: Discharge-stage relationship for (a) intact site, and (b) forested site

Appendix III. Rainfall and Discharge

Stream flow and rainfall patterns are plotted together for each storm runoff event to explore the response of the sites to rainwater inputs *(Figure IV-1 - Figure IV-3)*.

Intact site

August 2009

The first significant event started on 17 August 2009 at 3:00 am with a discharge of 0.06 m^3/s, which peaked after ~16 hours (0.34 m^3/s) and returned close to pre-event levels (0.08 m^3/s) after ~16 hours of peak discharge *(Figure IV-1a)*. This event resulted in a symmetrical hydrograph (each limb spanning ~16 hours) and lasted for about 32.5 hours. Between 14 August 2009 and 17 August 2009, a total of 34.8 mm rainfall is recorded with a peak rainfall recorded (9mm) on 17 August 2009 at 6:00am; a lag of ~13 hours between rainfall and discharge peaks is evident from this event. Such a lag reflects the prolonged dry period prior to the event, and it takes longer to establish sufficient hydrologic connectivity in a catchment to raise the hydrograph.

During a second distinguishable event on 20 August 2009, 5:30am (initial discharge-0.08 m^3/s) stream hydrograph peaked after ~16hrs to reach a maximum discharge at 0.54 m^3/s *(Figure IV-1a)*. Similar to the first event, this event lasted for ~31 hours. A total of 15.4 mm rainfall was recorded for two days (18 Aug 2009 - 20 Aug 2009). Maximum rainfall (2.2mm) was recorded on 20 Aug 2009, 9:00am; again, the lag between rainfall and stream flow peaks is about 12.5 hours. Interestingly, when a rainfall of 35 mm resulted in a hydrograph peak at 0.34 m^3/s during the first event (on 17/08/2009), only a rainfall of 15.4 mm sufficient to raise the hydrograph to 0.54 m^3/s during the second event (20/08/2009) which reflects the effect of antecedent soil moisture conditions.

In the above two events, hydrograph peaks were not single-peaked *(see Figure IV-1a)* and given the amount of time taken for them to last, they appear to be flushing events after a prolonged dry period.

09 July 2010

This event was onset on 9 July 2010 12:30 with a low summer flow (0.03 m^3/s) and reached maximum discharge (0.9 m^3/s) after ~3.5 hours *(Figure IV-1b)*. This event lasted for nearly 24 hours before reaching a close to minimum discharge (0.1 m^3/s) on 10 July 2010 at 12:30; however, sampling programme for this event ended on 9 July 2010 22:00 due to a tight field trip schedule. Rainfall between on 09 August 2010 lasted for 6 hours with a total of 11.4 mm recorded. Despite the hydrograph peak arrived relatively soon, it took longer (~21hours) for the flow to return to pre-event levels, which resulted in a positively skewed hydrograph.

07 April 2011

This event commenced on 07 April 2011 at 10:00 hours with 0.07 m^3/s discharge, which peaked ~ 9.5 hours after the onset and reached a maximum discharge (2 m^3/s) at 19:30 hours, and lasted for 19 hours producing a symmetrical hydrograph spanning 9.5 hours on each limb *(Figure IV-1c)*. Total rainfall recorded during this event is 8.2 mm. Given the wet-antecedent conditions in the catchment lag between rainfall and discharge peaks of only about one-and-a-half hour is observed.

Forested Site

August 2009

First event was onset on 17 August 2009 at 1:30 hours with a discharge of 0.02 m^3/s, which peaked by 12:00 noon (after ~10.5 hours) to reach a maximum 0.32 m^3/s and returned close to pre-event levels (0.04 m^3/s) after ~23 hours of peak discharge *(Figure IV-2a)*. This event lasted for about 33.5 hours. Between 14

August 2009 and 17 August 2009, a total of 34.8 mm rainfall is recorded with a peak rainfall recorded (9mm) on 17 August 2009 at 6:00 hours and a lag of ~6 hours (half that of a similar event in the intact site) between rainfall and discharge peaks is evident from this event. When this event is compared to an event on the same date in the intact site *(Figure IV-2a)*, lag time between discharge and rainfall peaks is halved and peak arrived ~6 hours sooner after the onset of the hydrograph. This suggests a flashy nature of the forested site relative to the intact site, this may be due to the rapid flowpaths (through rootzones, pipes etc) taken by the water *en route* to the stream (Brown et al., 1999; Holden and Burt, 2003).

A second event commenced on 20 August 2009, 3:30am with a 0.03 m^3/s initial discharge, and the hydrograph peaked after ~11hrs reaching a maximum of 0.27 m^3/s *(Figure IV-2a)*. Compared to the first event, this event lasted longer by ~5 hours. A total of 15.4 mm rainfall is recorded for two days (18 Aug 2009 - 20 Aug 2009). Maximum rainfall (2.2mm) was recorded on 20 Aug 2009 9:00am, similar to the first event, a lag time of ~6 hours between rainfall and stream flow peaks is evident for this event *(Figure IV-2a)*. In contrast to that observed in the intact site, in the forested site, maximum discharges (~0.32 m^3/s) are recorded during the first event rather than during the event that followed. This may probably because during the first event, rapid flowpaths generated the maximum flows while during the later event hydrological connectivity was being established in the catchment (that may change flowpaths of water) as is evident from the length of the event relative to the former event.

27 April 2010

This event was onset on 27 April 2010 at 15:30 hours with a minimum discharge of 0.01 m^3/s on the rising limb of the hydrograph, that peaked (0.1 m^3/s) after ~8.5 hours *(Figure IV-2b)*. This event lasted for nearly 28 hours, after

receiving a total rainfall of 5.6 mm. A lag time of 6 hours between discharge and rainfall peaks is apparent during this event.

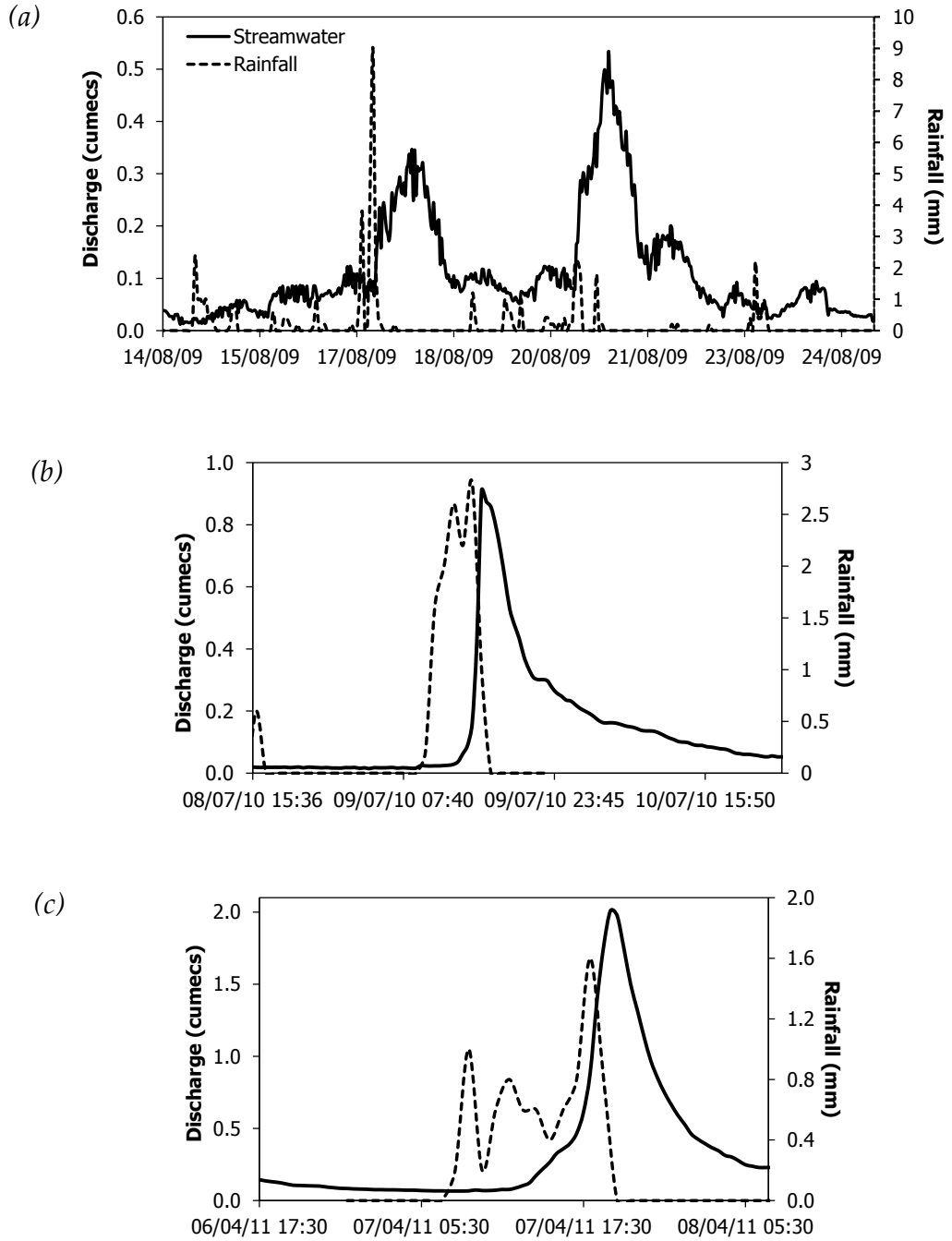

Figure 0.1: Plots showing changes in stream hydrograph with respect to rainfall received in the intact site, during runoff events: (a) August 2009, (b) July 2010, and (c) April 2011. Solid line – discharge (m^3s^{-1} sq km^{-1}); dashed line –rainfall (mm).

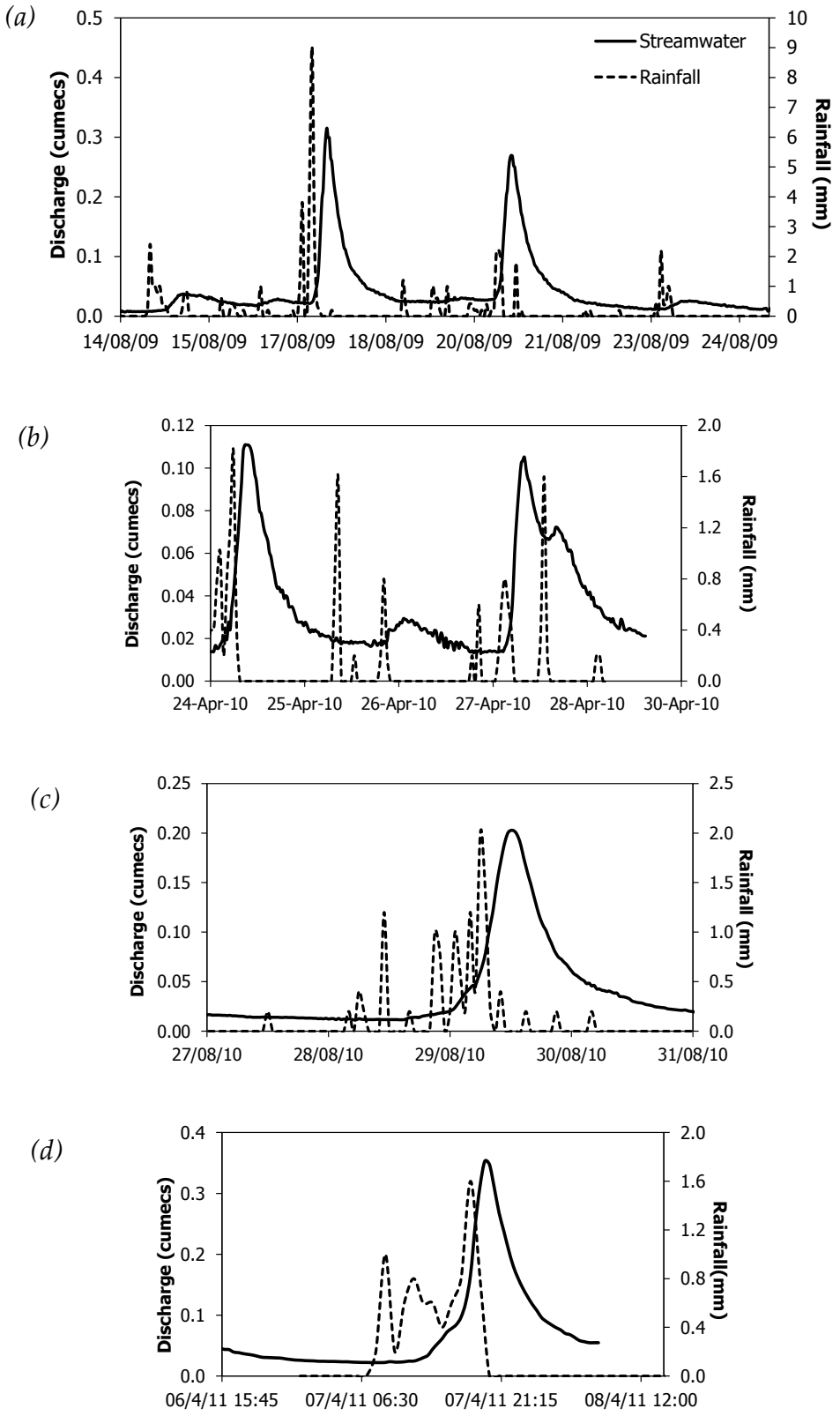

Figure 0.2: Plots showing changes in stream hydrograph with respect to rainfall received in the forested & felled sites, during runoff events: (a) August 2009, (b) April 2010, (c) August 2010, and (d) April 2011. Solid line – discharge (m^3s^{-1} sq km^{-1}); dashed line –rainfall (mm).

28 August 2010

This event started on 28 August 2010 at 14:30 hours *(Figure IV-2c)* with a discharge of 0.01 m^3/s, which reached a peak (0.2 m^3/s) after 21 hours and lasted for ~33 hours. Rainfall total for 48 hours prior to and during this event is 12.2 mm. A similar 6-hour lag time is seen between peak discharge and peak rainfall.

07 April 2011

This event commenced on 07 April 2011 at 11:00 am *(Figure IV-2d)*with an initial discharge of 0.02 m^3/s, and peak of hydrograph arrived about 8.5 hours after the onset of the event, which returned close to pre-event levels (0.06 m^3/s) after a further 10.5 hours. This event lasted for ~ 19 hours and a rainfall total for a 11 hour period (07 April 2011, 11:00 to 07 April 2011, 19:00) is recorded to be 8.2 mm. A lag time of only one-and-a-half hour is observed reflecting the wet-antecedent conditions in the catchment.

In this site, a general lag time of ~6 hours between peak rainfall and maximum discharge is observed for 4 out of 5 events. However, it still needs to be explored how this lag time would explain the temporal variability in DOC concentrations in this site.

Felled site

As discharge in the felled site is scaled using the data from forested site and the rainfall data is same for the entire River Dyke catchment, stream hydrographs (relative to rainfall) for this site are not being discussed here. It is assumed that a similar pattern to that of forested site would apply to this site as this site had also previously undergone drainage for forestry.

Appendix IV. Streamwater chemistry

Spatial and Temporal trends in Streamwater chemistry:

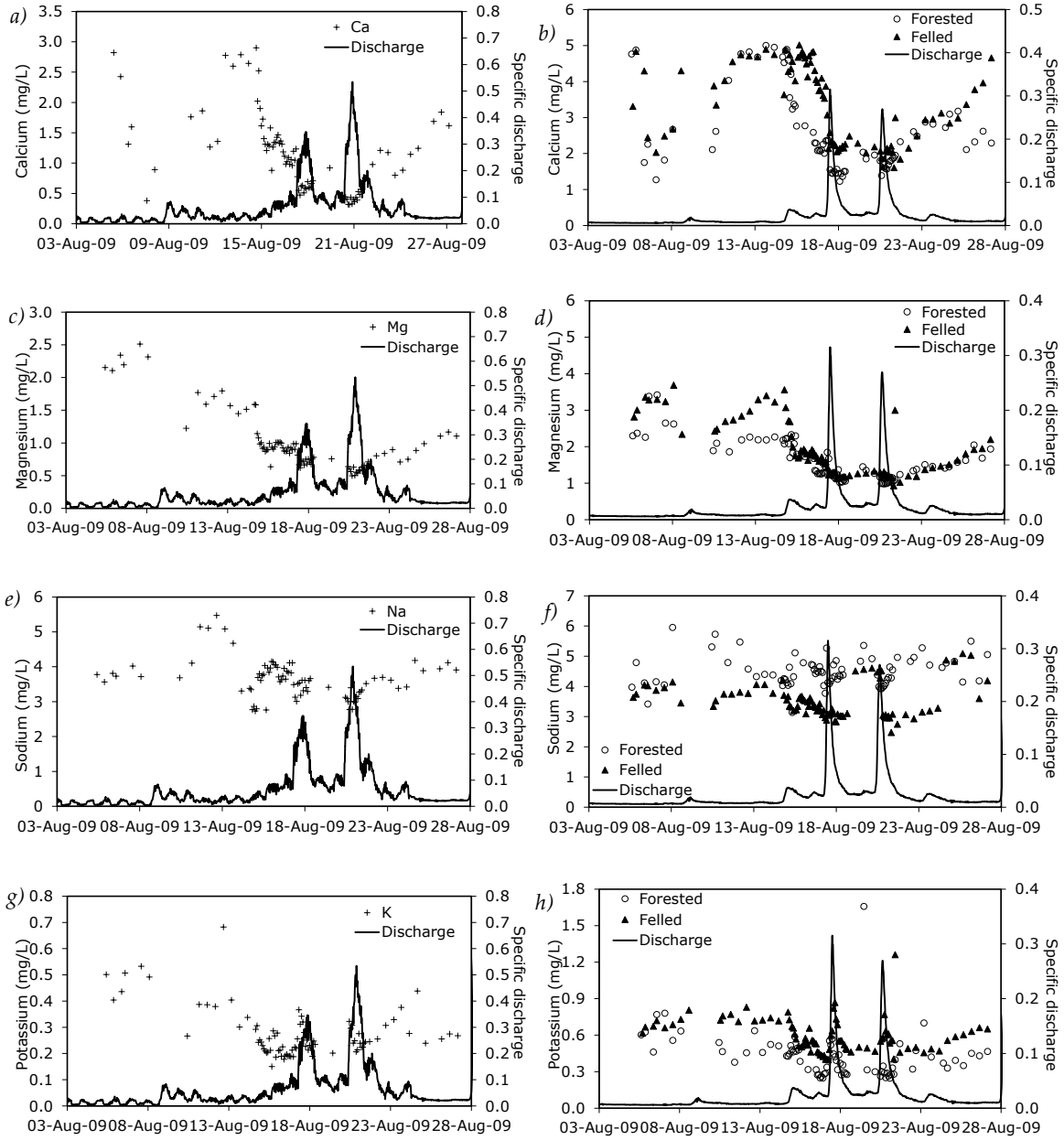

Figure 0.3: Plots showing variability in Ca, Mg, Na, K concentrations during summer events in 2009; (a, c, e, g & i) - intact peat, and (b, d, f, h & j) - forested and felled sites. Specific discharge is shown in $m^3s^{-1}km^{-2}$).

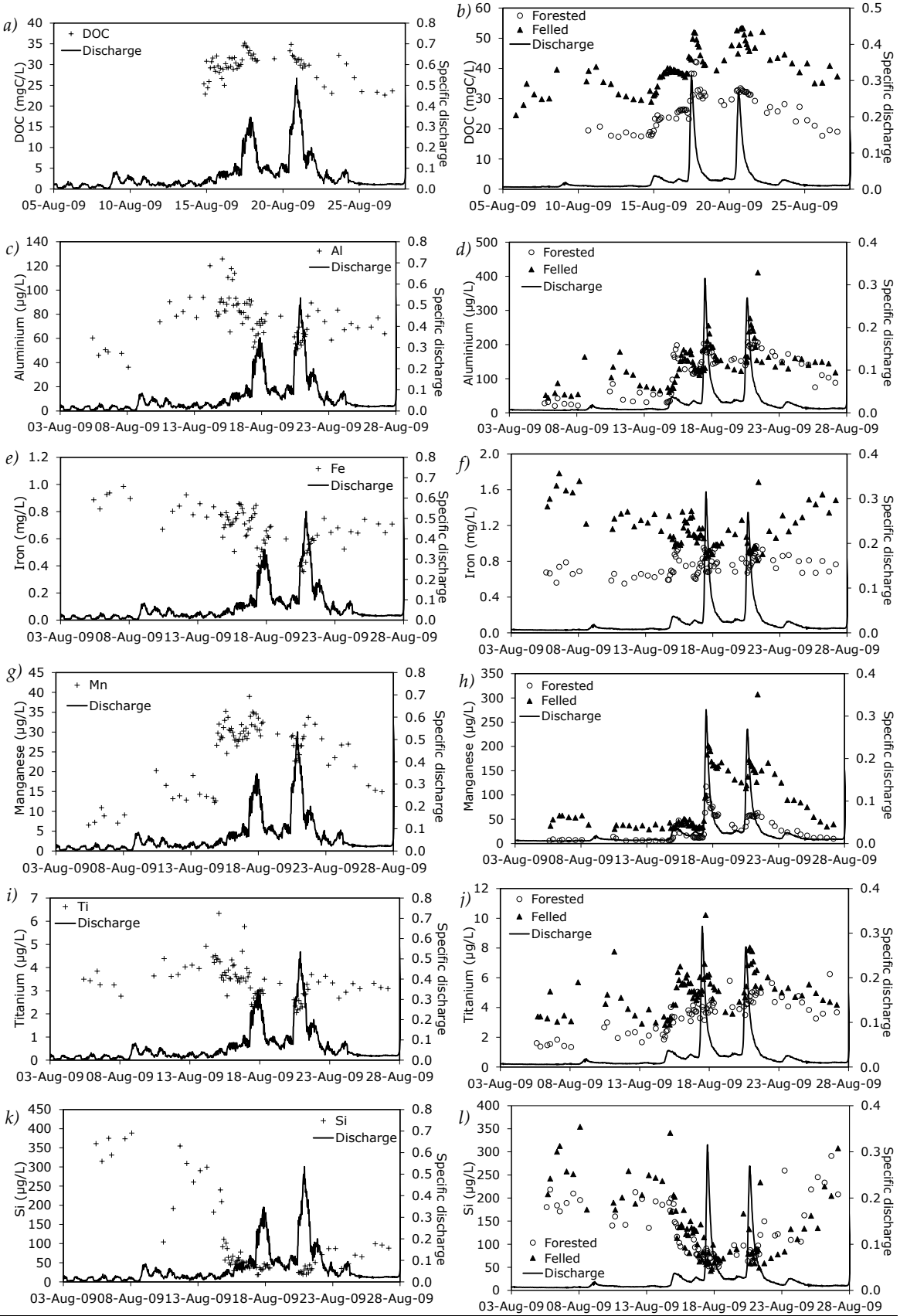

Figure 0.4: Plots showing variability in DOC, Al, Fe, Mn, Ti & Si concentrations during summer events in 2009. (a, c, e, g, i &k) - Intact peat, and (b, d, f, h, j & l) - Forested and Felled sites. Specific discharge is shown in m^3s^{-1} km^{-2}.

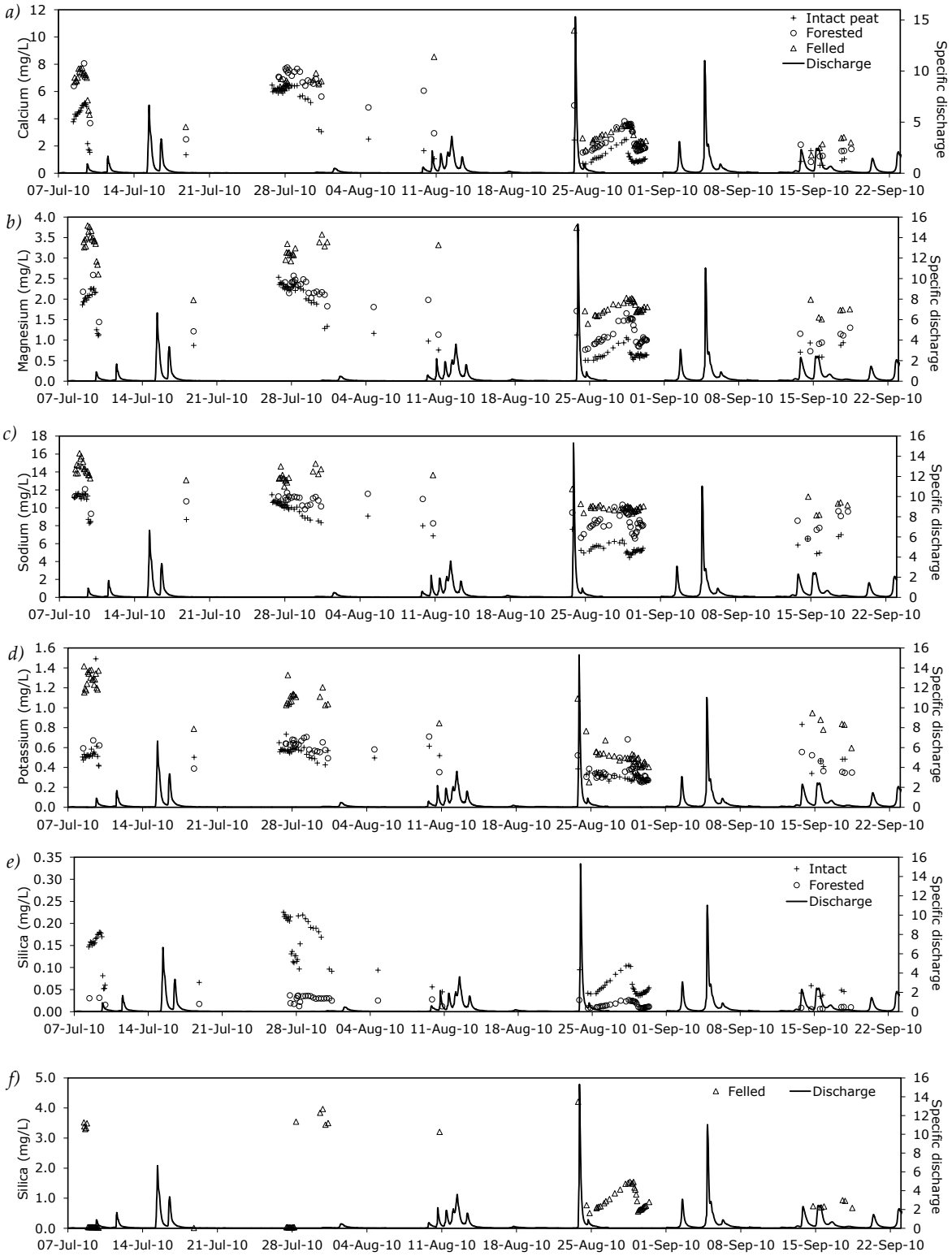

Figure 0.5: Plots showing variability in Ca, Mg, Na, K & Si concentrations with varying discharge, in three different landuses. Specific discharge is shown in m^3s^{-1} km^{-2}.

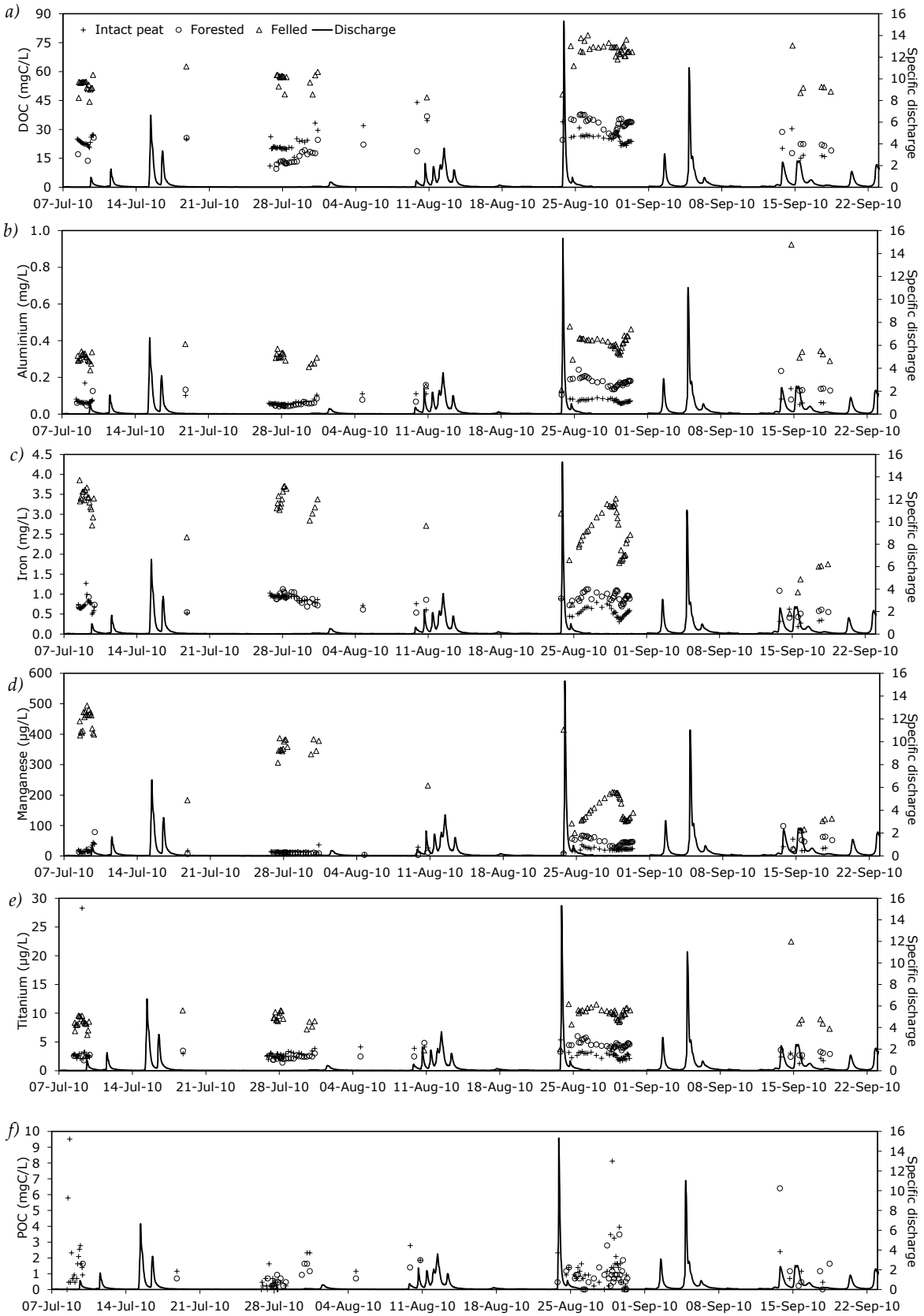

Figure 0.6: Plots showing variability in DOC, Al, Fe, Mn, Ti & POC concentrations with varying discharge, in three different landuses. Specific discharge is shown in m^3s^{-1} km^{-2}.

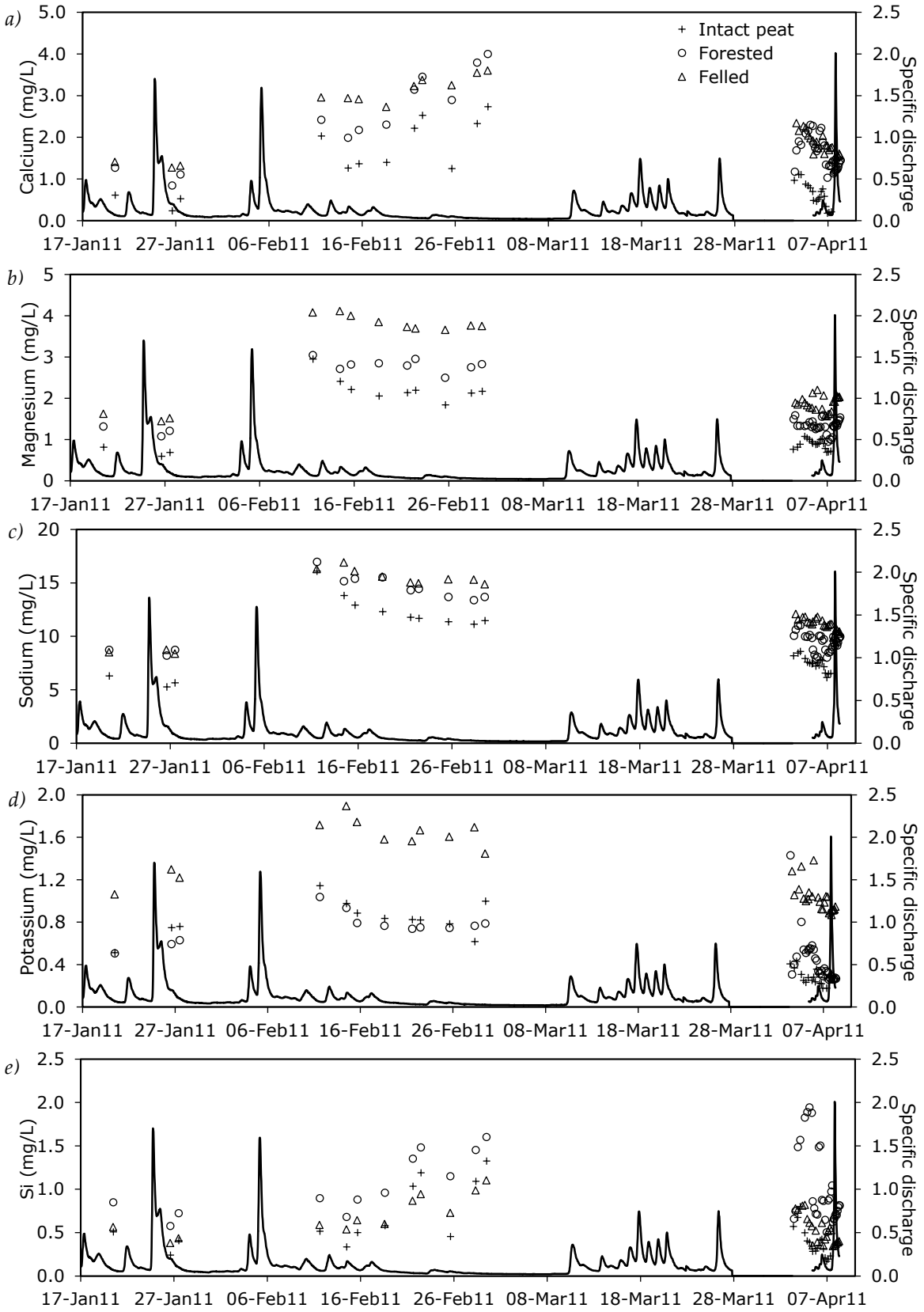

Figure 0.7: Plots showing variability in Ca, Mg, Na, K & Si concentrations during winter and spring events in 2011. Specific discharge is shown in m^3s^{-1} km^{-2}.

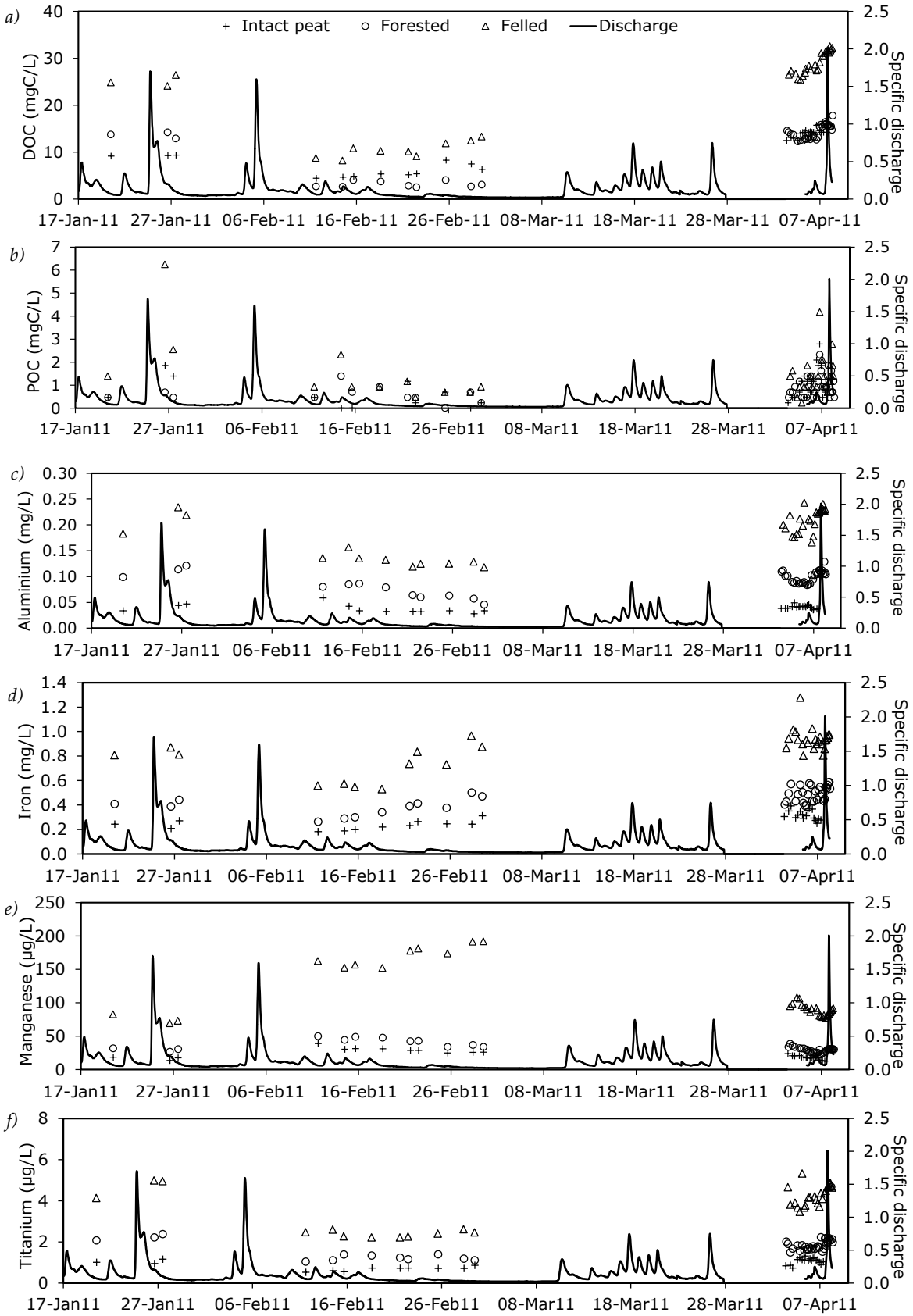

Figure 0.8: Plots showing variability in DOC, Al, Fe, Mn, Ti & POC concentrations with varying discharge during winter and spring events in 2011. Specific discharge is shown in m^3s^{-1} km^{-2}.

Factor Analysis

Factor analysis is a statistical technique in which the inter-relationships within a set of *m* variables reflect the correlations of each individual variable with *p* mutually uncorrelated underlying factors (Davis, 1986). Simply, the factors are the linear combinations of the original variables. Multiplying an *m X p* matrix by its transpose will produce an *m X m* matrix from which eigenvalues and eigenvectors are extracted.

R-mode technique adopted for this study utilizes principal components and the eigenvalues and eigenvectors (vectors of unit length) are extracted from correlation matrix of the normalized data matrix. The underlying *factors* are then derived by multiplying each element in the eigenvector by the square root of the respective eigenvalue (Davis, 1986). Thus, the resultant *factor* (a vector) is proportional to the amount of variance it represents. The elements in the factor matrix are the *factor loadings* that are proportional to the amount of variance contributed by that variable, and its size represents a measure of the amount of variance of each variable explained by that factor (Davis, 1986).

The *Q-mode technique* adopted in this study is similar to R-mode analysis, except for that the role of samples and variables are interchanged. That is, Q-mode analysis takes into account the inter-relationships between samples, rather than variables. The normalized data matrix with *n* samples and *m* variables (*n X m*) is used to produce an *n X n* similarity matrix that contain similar sample pairs based on the way they respond to the variables. Eigenvalues and eigenvectors are extracted from the similarity matrix (n X n). *Factors* are then produced using the same procedure applied in R-mode analysis and the resultant factor matrix contains *factor loadings*. In this case, the size of a resultant factor loading is proportional to the amount of variance of each sample explained by that particular factor (Davis, 1986). A factor loading close to ± 1.0 indicates a strong relationship between the factor and the variable, and

loadings that are closer to zero have less significant correlation. Generally, the first few factors that explain most of the total variance are retained, and rest of the factors can be excluded from further analysis without much loss of information. In this study, factors with eigenvalues greater than 1 are retained (Kaiser Criterion). In order to aid better interpretation of results, sometimes factor axes are rotated orthogonally or obliquely to move to positions so that projections from each variable onto the factor axes are more readily interpretable (Davis, 1986). The retained factors were then rotated using the Varimax method (Comrey and Lee, 1992; Davis, 1986) to attain simple structure for easy interpretation.

A simultaneous R-mode and Q-mode factor analysis was carried out using Minitab® (a statistical package) on the transformed data matrix. Once the factor matrices with factor loadings for all variables and samples are derived, the original data can be plotted in the new factor space to compare the relationship between sample and variable factor loadings. Since the factors derived are mutually orthogonal to each other in a multidimensional factor space, any two factors can be displayed as perpendicular axes in two-dimensional space (Kovach, 1995). That means, it is possible to plot the original variables as a simple scatter plot onto a two-dimensional space with any two of the new factors (Walden and Smith, 1995). Usually, variables (or samples) that are highly correlated, and/or respond similarly to the hydrological changes plot in close proximity within the factor space. A common set of factors from R-mode and Q-mode analysis are derived such that for any two given factors, variable and sample factor loadings can be plotted in the same two-dimensional factor space.

There are certain criticisms about factor analysis such as selection of rotation methods and the preconception of the modeller in relation to the number of factors to be retained (Davis, 1986; Swan and Sandilands, 1995).

However in this study, as the un-rotated solution was not readily interpretable, the most widely used 'Varimax' rotation method was adopted to aid better interpretation of the results, and the factor extraction method uses a principal component approach, where the number of factors to be retained is not necessarily known prior to analysis. In this method, all eigenvectors and eigenvalues of a correlation matrix are extracted and the less significant ones of the extracted factors are then discarded after careful inspection; in the present study, this has coincided with the factors whose eigenvalues are greater than one.

(a)

Variable	*Factor1*	*Factor2*	*Factor3*	*Factor4*	*Factor5*	*Factor6*	*Factor7*	*Factor8*	*Factor9*	*Communality*
DOC	**0.860**	0.167	0.003	-0.215	0.106	0.414	0.051	-0.009	0.016	1.00
Ti	**0.936**	-0.136	0.009	-0.111	0.198	-0.048	-0.034	-0.223	0.016	1.00
Al	**0.950**	0.060	-0.108	-0.016	-0.085	-0.139	-0.094	0.216	0.015	1.00
Fe	**0.802**	-0.411	0.147	-0.076	-0.174	0.078	0.352	-0.011	-0.012	1.00
Mn	0.009	0.254	**-0.949**	-0.112	0.150	-0.002	-0.017	0.006	0.003	1.00
Ca	0.191	**-0.911**	0.215	0.199	-0.105	0.011	0.012	-0.016	0.187	1.00
Mg	-0.064	**-0.875**	0.192	0.257	-0.26	-0.065	0.043	-0.007	-0.231	1.00
Na	-0.050	-0.450	0.291	0.374	**-0.754**	-0.027	0.027	0.016	-0.006	1.00
K	-0.232	-0.388	0.142	**0.845**	-0.245	-0.036	-0.011	0.005	-0.004	1.00
Variance	*3.2593*	*2.2329*	*1.121*	*1.0372*	*0.8176*	*0.2057*	*0.1396*	*0.0974*	*0.0893*	*9.00*
% Var	*0.362*	*0.248*	*0.125*	*0.115*	*0.091*	*0.023*	*0.016*	*0.011*	*0.01*	*1.00*

(b)

Variable	*Factor1*	*Factor2*	*Factor3*	*Factor4*	*Factor5*	*Factor6*	*Factor7*	*Factor8*	*Factor9*	*Communality*
DOC	**0.803**	-0.073	0.273	0.235	0.319	-0.067	0.056	-0.012	0.332	1.000
Ti	**0.849**	-0.202	0.162	0.228	0.159	-0.058	0.183	0.312	-0.024	1.000
Al	**0.518**	**-0.593**	0.185	0.049	0.198	-0.221	**0.502**	0.045	0.023	1.000
Fe	**0.926**	0.001	-0.009	-0.178	-0.194	0.171	-0.042	-0.170	-0.111	1.000
Mn	0.097	**-0.974**	0.074	0.001	0.162	-0.096	0.027	0.014	0.006	1.000
Ca	0.160	**0.522**	-0.310	-0.127	-0.407	**0.641**	-0.112	-0.018	-0.018	1.000
Mg	-0.105	0.348	-0.371	-0.230	**-0.793**	0.203	-0.072	-0.031	-0.035	1.000
Na	-0.063	0.015	-0.164	**-0.973**	-0.135	0.054	-0.019	-0.020	-0.021	1.000
K	-0.192	0.121	**-0.917**	-0.189	-0.234	0.118	-0.050	-0.017	-0.023	1.000
Variance	*2.5796*	*1.7559*	*1.2421*	*1.1921*	*1.0976*	*0.5633*	*0.3122*	*0.1306*	*0.1266*	*9.00*
% Var	*0.287*	*0.195*	*0.138*	*0.132*	*0.122*	*0.063*	*0.035*	*0.015*	*0.014*	*1.00*

Table II: Factor loading results from R-mode analysis for (a) intact site, and (b) forested site. Factor loadings > 0.5 and < -0.5 are shown in bold to emphasize the significance of the variable on the factor(s).

(a) *Variable*	*Factor1*	*Factor2*	*Factor3*	*Factor4*	*Factor5*	*Factor6*	*Factor7*	*Factor8*	*Factor9*	*Communality*
DOC	**0.819**	-0.128	-0.057	0.398	0.110	0.016	-0.136	-0.346	0.017	1.000
Ti	**0.973**	-0.058	0.019	0.062	0.162	0.026	-0.041	0.077	0.104	1.000
Al	**0.846**	0.116	0.385	-0.065	0.231	0.044	0.075	0.057	-0.232	1.000
Fe	**0.530**	**-0.612**	0.290	0.109	0.273	-0.060	-0.403	-0.084	0.020	1.000
Mn	0.349	-0.160	0.236	-0.254	**0.855**	-0.002	-0.038	-0.012	-0.007	1.000
Ca	0.058	**-0.991**	-0.004	-0.055	0.096	0.053	0.009	-0.009	0.005	1.000
Mg	-0.197	**-0.707**	0.439	-0.287	0.010	-0.429	-0.049	0.008	0.008	1.000
Na	0.184	-0.146	**0.903**	-0.281	0.217	-0.040	-0.037	0.006	-0.007	1.000
K	-0.156	-0.121	0.268	**-0.916**	0.219	-0.039	0.015	0.019	-0.006	1.000
Variance	*2.838*	*1.951*	*1.372*	*1.246*	*1.002*	*0.196*	*0.194*	*0.137*	*0.065*	*9.000*
% Var	*0.315*	*0.217*	*0.152*	*0.138*	*0.111*	*0.022*	*0.022*	*0.015*	*0.007*	*1.000*

(b) *Variable*	*Factor1*	*Factor2*	*Factor3*	*Factor4*	*Factor5*	*Factor6*	*Factor7*	*Factor8*	*Factor9*	*Communality*
DOC	**0.963**	0.003	0.099	0.028	-0.122	-0.109	-0.009	0.187	0.029	1.000
Ti	**0.928**	0.181	0.036	-0.086	-0.188	0.111	-0.010	-0.223	0.032	1.000
Al	**0.780**	0.067	-0.168	-0.139	-0.373	0.446	0.014	-0.026	0.018	1.000
Fe	**0.776**	0.470	-0.204	-0.091	-0.210	-0.059	0.049	0.008	-0.278	1.000
Mn	0.494	0.037	-0.077	-0.257	**-0.825**	0.050	0.017	-0.003	-0.017	1.000
Ca	0.186	**0.948**	-0.144	-0.153	0.033	0.007	-0.145	-0.016	0.006	1.000
Mg	0.073	**0.817**	-0.296	-0.345	-0.127	0.034	0.319	0.001	-0.036	1.000
Na	-0.007	0.262	**-0.944**	-0.186	-0.062	0.028	0.015	-0.003	-0.013	1.000
K	0.078	0.397	-0.248	**-0.847**	-0.238	0.032	0.014	-0.007	-0.008	1.000
Variance	*3.288*	*2.052*	*1.148*	*0.996*	*0.990*	*0.232*	*0.126*	*0.086*	*0.082*	*9.000*
% Var	*0.365*	*0.228*	*0.128*	*0.111*	*0.110*	*0.026*	*0.014*	*0.010*	*0.009*	*1.000*

Table III: Factor loading results from R-mode analysis for (a) felled site, and (b) pooled data. Factor loadings > 0.5 and < - 0.5 are shown in bold to emphasize the significance of the variable on the factor(s).

Table IV: Descriptive statistics of estimated groundwater and soilwater proportions using End-member mixing analysis (EMMA)

	%Ground water			**% Soilwater**					
Site	*Min*	*Max*	*Mean*	*Min*	*Max*	*Mean*	*SE Mean*	*Std Dev*	*N*
Intact	36.6	103.5	55.3	-3.5	63.4	44.7	1.23	19.1	241
Forested	36.2	113.2	56.0	-13.2	63.8	44.0	1.19	17.7	220
Felled	35.0	147.4	61.9	-47.4	65.0	38.1	1.51	22.1	215